

Thesis/
Reports
Moore,
B. C.

THE ENVIRONMENTAL FATE OF TRICLOPYR IN SOILS
FOLLOWING FOREST SITE PREPARATION APPLICATIONS

BY

BARRY C. MOORE AND BIJAN DANESH

Final for Coop Agreement No.:
22-C-6-INT-079 with Wash. State Univ.
FS Contact: Barry C. Moore
Coop Contact: Alan E. Harvey

THE ENVIRONMENTAL FATE OF TRICLOPYR IN
SOILS FOLLOWING FOREST SITE PREPARATION
APPLICATIONS

Barry C. Moore and Bijan Danesh

March 13, 1989

State of Washington Water Research Center
Washington State University
Pullman, WA 99164-3002

ACKNOWLEDGEMENTS

The authors sincerely thank the numerous people who have made contributions to this work. Mr. Dan Miller of the Potlatch Corporation spent much time assisting with the location of a suitable study site. Dr. Rene Mangin offered advice and assistance in the initial study preparation. Ms. Vanelle Carrithers of the DOW Chemical Company provided triclopyr standards and formulations. Some of the staff of the State of Washington Water Research Center, Ms. Sandra Johnson and Ms. Diane Weber, provided invaluable contributions to the project in budget tracking and in editing the manuscript, respectively. Dr. William H. Funk, Director of the State of Washington Water Research Center, advised the authors and made available the services of his staff and other resources throughout the course of the project.

INTRODUCTION

Triclopyr is a broad spectrum herbicide introduced in 1973 by the Dow Chemical Company. While triclopyr has certain attributes that make it the herbicide of choice for many applications, the 1979 suspension of use of 2,4,5-T and Silvex by the U.S. Environmental Protection Agency has increased interest in triclopyr, which shows reasonably similar vegetation control characteristics. This interest is particularly pronounced in the forest products industry, where a suitable substitute for the suspended product has been the subject of much research and debate. 2,4,5-T had very widespread use in forestry, and the potential application of triclopyr for vegetation management, especially in control of hardwoods in conifer sites, is great. The study described in this report was designed to characterize the environmental fate of triclopyr following applications for vegetation management for forest site preparation in the Northwest, so that a reasonable assessment of the risks associated with its use in such applications can be performed. Of primary interest for the studies described here was the expansion of a very limited research base on triclopyr under actual environmental conditions in order to evaluate the applicability of data gathered under laboratory conditions. A review of the extant literature on triclopyr is also included. Before proceeding with the literature review and with the project methods and results, a discussion of the approach taken in the research described here in developing data for risk assessment is appropriate.

As with any chemical which will be introduced into the environment, there is concern that the impacts on non-target organisms be within acceptable ranges. The informed assessment of risks to non-target organisms associated with use of chemicals in the environment involves a knowledge of the toxicity of the compound to the organisms and a reasonable estimate of their exposure to the chemical. The first step in chemical risk assessment, the evaluation of toxicity, has been relatively well defined, with numerous standard tests to evaluate toxic properties of a chemical to a wide range of organisms. These tests include many procedures aimed at evaluating the probable toxic properties to humans. Standardized tests allow for comparison of new chemicals with the characteristics of chemicals in use for longer periods of time and so offer a relative measure of the safety of the new product.

The second step in chemical risk assessment, evaluation of the probable levels of exposure of non-target organisms to the compound of interest, has a methodology which is neither as well-defined nor as standardized as the assessment of toxicity. However, evaluation of exposure can be approached in a conceptual manner which

allows a systematic methodology. There has been considerable progress in recent years in developing methods for the assessment of environmental risks associated with exposure, and some basic principles seem to have evolved.

Exposure is a function both of the concentration to which the organism of interest is subjected and the length of time it remains in contact with the chemical. The conceptual approach for chemical risk assessment has been to define the environment as a series of compartments, such as air, soil, and water, with delineation of the non-target organisms into the appropriate compartments in which the exposures will occur. The task then becomes defining a) the pathways and rates of exchange, or migration, of the chemical between the various compartments, b) the persistence or residuality (Laskowski et al., 1982), and c) the rate of exchange between the biotic and abiotic compartments. The first two tasks define the environmental fate of the product, while the last task involves the actual risk analysis which seeks to evaluate the exposure and response of the biota within the context of the toxicity of the product.

The actual environment is, of course, extremely heterogeneous and complex. Therefore, two trends in chemical risk assessment have recently evolved. One trend is to attempt to correlate the environmental properties of chemicals with some basic chemical and physical properties which lend themselves to quantification. The other approach has been to actually monitor the environmental components in small scale field tests in such a manner as to produce data which may be extrapolated to the more general case. Both approaches have their strengths and limitations.

The correlation of chemical and physical properties with environmental fate assumes that there is an underlying continuity in the interactions of chemicals with the environment that is determined by their chemical and physical properties. Much work has been performed on the correlation of partitioning coefficients to environmental behavior, with particular emphasis on K_{ow} , the octanol water constant, K_w , the water solubility constant, and K_{oc} , the soil adsorption constant. For example, Kenaga (1980), using some feeding studies, was able to demonstrate direct correlation between the K_{ow} of 23 pesticide compounds and the residual concentration of the compounds in beef fat. He also demonstrated an inverse correlation between the water solubility and the residual concentration of the compounds in beef fat. While these results are very interesting, large uncertainties regarding the correlation of partitioning coefficients with other environmental behaviors remain.

In the use of monitoring and actual field applications, there is the disadvantage

of interpreting data which reflects the interactions of many different processes. There is also the problem of extrapolating from the specific to the more general case which arises because of the vast array of environments where chemicals might be expected to be utilized. However, actual field tests may show unexpected differences in behavior in the environment versus those in the laboratory. Field tests are particularly useful when knowledge of processes gained from the laboratory can be applied to the interpretation of field data. This may allow for the isolation of processes of interest in the field which do not lend themselves to laboratory analysis and gives a truer picture of the *composite* results of interacting processes.

The research approach taken in the present study has been to use the knowledge of the physical and chemical properties of triclopyr, combined with some actual field applications and subsequent monitoring, to produce information applicable for assessment of the risk to non-target organisms associated with its use in certain forestry applications.

LITERATURE REVIEW

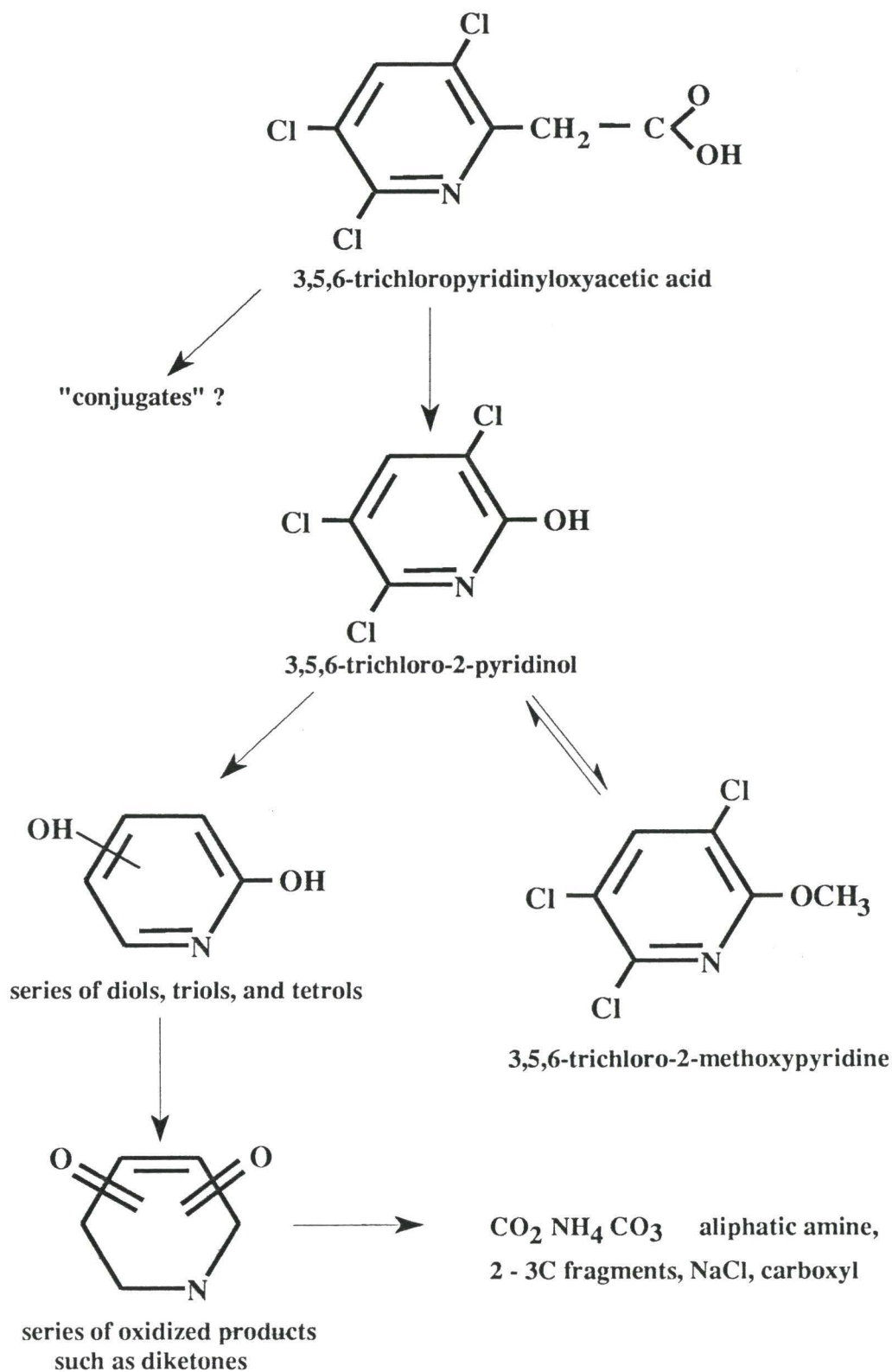
General Information and Chemical and Physical Properties

Triclopyr is the common name for 3,5,6- trichloro -2- pyridyloxyacetic acid (IUPAC) (alt. [(3,5,6- trichloro -2- pyrininyl)oxy]acetic acid) (Figure 1). The compound was registered by the Dow Chemical Company in 1973 under the code number, Dowco 233, registration number 55335-06-3. The formula weight is 256.5. Triclopyr is also formulated as a water soluble, triethylamine salt (formula weight 371.7) and as an oil-soluble butoxyethyl ester (formula weight, 356.6; registration number, 64470-88-8).

At 25°C, triclopyr is a fluffy, colorless solid. Under normal dark storage conditions, the compound is stable and resistant to hydrolysis, but it will photolyze rapidly when exposed to ultraviolet light. The half-life of triclopyr under photolytic conditions is reported at less than 12 hours. The melting point is 148° to 150°C., and decomposition occurs at 290°C (Worthing, 1983).

Triclopyr is acidic, with a dissociation constant (pK_a) of 2.68. The compound has a low volatility, with a vapor pressure of 168 μ Pa (1.3×10^{-6} mm-Hg) at 25°C. Solubility in water (K_w) is variously reported as 430 to 440 ppm (Laskowski et al.,

Figure 1. Structural formulae of triclopyr and its breakdown products, showing probable degradational sequence (after Marshall and Roberts, 1978).



1982; Worthing, 1983). Solubilities of triclopyr in a number of solvents at 25°C are given in Table 1.

Table 1. Solubility of triclopyr in various solvents at 25°C (Weed Science Society of America, 1983).

SOLVENT	PPM	% SOLUBILITY
Acetone	989,000	98.9
Acetonitrile	126,000	12.6
Benzene	2,730	2.73
Chloroform	2,730	2.73
n-Hexane	410	0.041
n-Octonal	30,700	30.7
Xylene	2,790	2.79
Water	430	.043

Formulations and Product Information

Triclopyr is marketed as Garlon (trademark of the Dow Chemical Company). The water-soluble triethylamine salt formulation is sold as Garlon 3A and the butoxyethyl ester is sold as Garlon 4. These products contain 3 and 4 pounds per gallon of active ingredient, respectively. More recently, the oil-soluble, water-emulsifiable ester has been marketed as Grazon ET (trademark of the Dow Chemical Company) (Jacoby and Meadows, 1984). Triclopyr has been applied in mixtures with 2,4-D, picloram, and 3,6-dichloropicolinic acid. Garlon is usually applied as standard water solutions or as oil-in-water emulsions, but work on the use of inverting adjuvants with Garlon showed improved results for some applications, in particular, the hovering helicopter method for bigleaf maple (*Acer macrophyllum*) control (King et al., 1983).

Applications

Triclopyr affords good control of a wide spectrum of broad-leaved plants at normal rates of application (approximately 1 to 4.5 kg/ha) (Boyd et al., 1985). The herbicide was originally developed for vegetation maintenance on industrial sites and utility rights-of-way (McKellar et al., 1982). Because of the wide range of species controlled by triclopyr, the herbicide has been used or suggested for use for most types of noncrop weed management applications. Some of the most promising applications

involve forestry and rangeland uses. Garlon formulations have been shown to be effective on honey mesquite (*Prosopis juliflora*), a particularly common problem species in southwestern range areas. In forestry, Garlon has been used for site preparation and conifer release except over pines and for cut stump and basal sprays (Boyd et al., 1985). Garlon has been used in aerial and ground sprays using water or oil carriers and has been shown to be effective when applied as an invert emulsion. The invert emulsion was investigated primarily in conjunction with the hovering helicopter method for control of bigleaf maple (*Acer macrophyllum*) in Pacific Northwest forest applications (King et al., 1983).

An extensive summary of the phytotoxicity of Garlon in different formulations and in combination with other herbicides to weed and conifer species of the Inland Northwest area may be found in Boyd et al. (1985). Other studies, not already cited, on the effectiveness of triclopyr formulations for various vegetation management applications include the following: Haagsma (1975), Bovey and Meyer (1981), Bovey et al. (1981), Byrd et al. (1975), Holt et al. (1985), McCormack (1979), Jacoby and Meadows (1983), Meyer and Bovey (1985), Miller and Pope (1981, 1982a and b), and Miller and Pope (1983).

Some preliminary investigations have been conducted on the efficacy of triclopyr for aquatic weed control, particularly in management of Eurasian water milfoil (*Myriophyllum spicatum*) (Getsinger and Westerdahl, 1984). The herbicide shows promise for aquatic applications, and the manufacturer is conducting research pursuant to registration of triclopyr for aquatic use (V. Carouthers, Dow Chemical Company, personal communication).

Uptake, Translocation, and Metabolism in Plants

Triclopyr is readily taken up by plants through both the roots and foliage and is readily translocated throughout the plant. Currently, information on the metabolism of triclopyr in plants is not available, however, measurements of triclopyr residues in plants following treatment have been done. These data indicate possible relationships between the rate of plant metabolic activity and adsorption of triclopyr, but direct correlations have not been drawn.

The physical surface properties of leaves determine the extent to which foreign substances will penetrate the foliage. The waxy cuticle, which is hydrophobic and continuous over the entire outer surface of the epidermal layers, is the major impedi-

ment for free movement of substances into leaves. The pattern of leaf venation, the size and shape of underlying epidermal cells, the presence of hairs and the quantity, configuration and density of surface wax deposits are important leaf surface characteristics. Structural differences in leaves occur between species as well as in plants of the same species growing in different environments. The different ages of leaves on the same plant and the upper and lower surfaces of the same leaves also have structural differences. Certain regions or structures on leaves have been cited as the preferential site of uptake (Morrison and Cohen, 1980). These include areas over the veins, the base of the hairs and the guard and subsidiary cells of the stomata.

The primary function of the root is to take up water and nutrients. The structural characteristics of plant roots differ between species but all function as absorbing organs. Typically, roots have a high surface to volume ratio with a region, often between 5 and 50 mm from the root tip, which preferentially absorbs water and solutes (Morrison and Cohen, 1980). Uptake in roots is either active (requires the expenditure of metabolic activity) or passive (includes absorption, diffusion, and mass flow). Movement (translocation) of solutes through roots may occur either in the living symplast (total continuum of living protoplasm confined within the cell membrane) or the non-living apoplast (system of non-living interconnected cell walls and intercellular spaces including mature xylem vessels) or both. Apoplastic transport is usually associated with passive uptake. Substances which move apoplastically are transported upward in the plant and accumulate at the tips and margins of leaves. Symplastic transport is usually associated with active uptake processes and may move either upward or downward in the plant following a source to sink pattern. Sources are commonly regions of high photosynthetic activity (such as mature leaves) and sinks are regions of active growth (meristems of roots and shoots, storage tissues in roots and stems, newly expanding leaves, axillary buds and developing fruits).

The efficiency of transport in plants varies according to species and depends on the rate at which foreign substances are absorbed, the age and position of the source relative to the sink, the biosynthetic activity of the sinks and a range of environmental factors including temperature, light and moisture supply (Morrison and Cohen, 1980). An increase in temperature usually results in greater absorption and translocation of foliar-applied chemicals. This may be due to physical changes in the cuticle, lowering its penetration potential, or to an increase in the metabolism of the plant. High humidity may increase stomatal openings or improve cuticular penetration, both of which influence the rate of uptake. Increasing the amount and intensity of light increases the photosynthetic activity which results in a more rapid movement of carbohydrates from

the leaves. During the growing season, the efficiency of uptake is reduced with increasing leaf age.

Radosevich and Bayer (1979) used ^{14}C -labeled triclopyr applied to the foliage to study the effect of temperature and photoperiod on the translocation rate. Light and temperature play an important role in the efficiency of a herbicide due to their influence on carbohydrate production and transport. The maximum rate of translocation in a variety of plants occurred under conditions of warm temperatures and long photoperiod days. These conditions favor photosynthate production, transport, and meristematic activity. Isolation analysis of ^{14}C showed little metabolism of triclopyr. It was concluded that mobility of triclopyr in plants is due to specific structural or physiological differences between species as well as environmental conditions studied.

Triclopyr is readily taken up by roots and leaves of plants (Sassman et al., 1984). Radosevich and Bayer (1979) observed that triclopyr was rapidly translocated following uptake in a number of species and was enhanced by warm temperatures and long photoperiods. Translocation from roots was less than that from leaves (Bovey et al., 1979, 1983; Radosevich and Bayer, 1979; Bovey and Mayeux, 1980a and b). Residues of triclopyr in the treated plants were highest in the stems, with intermediate levels remaining in the leaf tissues (Bovey et al., 1979, 1986; Radosevich and Bayer, 1979; Bovey and Mayeux, 1980a and b). Triclopyr appears to accumulate principally in the meristematic tissue (Bovey et al., 1979, 1983; Bovey and Mayeux, 1980a, 1980b; Gorrell, 1980; Gorrell et al., 1979; Engle and Bonham, 1980; King and Radosevich, 1979; Radosevich and Bayer, 1979), and residue concentrations in the vegetation were found to be proportional to the rates of application (Siltanen et al., 1981).

King and Radosevich (1979) studied leaf surface characteristics and how they affected the absorption of ^{14}C -labelled triclopyr in tanoak. Penetration into the adaxial (upper) and abaxial (lower) leaf surface was compared using immature and mature leaves. Greater amounts of ^{14}C triclopyr were absorbed by the immature leaves than the mature leaves and by abaxial than adaxial surfaces. Autoradiographs of treated leaves indicated that no ^{14}C activity moved from the point of application indicating there was little degradation of ^{14}C triclopyr. Enhanced absorption was associated with stomatal densities. There were greater densities of stomata on the immature leaves than on the mature. In summary, greatest absorption occurred when leaf surfaces had low amounts of cuticular wax, high density of stomates, and thin cuticular membranes.

Absorption, translocation and concentration of triclopyr in honey mesquite has been studied in greenhouse grown plants (Bovey et al., 1983) and in field grown plants (Bovey et al., 1983; Bovey et al., 1986). Concentrations of triclopyr in both studies were determined in the phloem (living tissue; translocates substances in both directions) and xylem (mostly dead cells; translocates water and nutrients from the roots to the stems). In the greenhouse studies (Bovey et al., 1983), both the ester and amine formulations were used. Initial absorption was shown to be highest for the ester formulation; however, after 24 hours 66% of the ester formulation had been absorbed and 72% of the amine formulation had been absorbed. Triclopyr was rapidly transported from the treated leaf to other parts of the plant. Concentrations of triclopyr recovered from stems of field-grown honey mesquite ranged from 0.16 to 0.72 $\mu\text{g/g}$ fresh weight in phloem and from 0.04 to 0.20 $\mu\text{g/g}$ in xylem 3 and 30 days after broadcast sprays of the butoxyethanol ester at 1.12 kg/ha (Bovey et al., 1983). Bovey et al (1986) did more extensive studies to determine the concentrations of triclopyr in phloem and xylem tissues from stems of the upper canopy and base of field-grown honey mesquite 3 and 30 days after treatment. Highest concentrations for both 3 and 30 days after treatment were detected in the upper stem phloem (0.8 $\mu\text{g/g}$ fresh weight) compared with concentrations in basal stem phloem (0.4 $\mu\text{g/g}$), upper stem xylem (0.2 $\mu\text{g/g}$) and basal stem xylem (0.1 $\mu\text{g/g}$).

Gorrell (1980) studied the translocation, fate and influence on carbohydrate metabolism of various herbicides in horsenettle roots. Triclopyr applied at 3.36 kg/ha showed evidence of root accumulation for 16 days. After 16 days little or no metabolism was evident in either the shoot or root. The total non-structural carbohydrate in foliage and roots was reduced with increasing rates of foliage applied triclopyr. The fleshy roots of control plants contained 53% total non-structural carbohydrate and 45% starch. The starch of plants treated with triclopyr decreased to between 15 and 21%.

Siltanen et al. (1981) reported residue levels of 0.3, 0.8, and 1.9 ppm, corresponding respectively to application rates of triclopyr at 0.25, 0.75, and 2.25 kg/ha in cowberries, 30 days after treatment. Residues for bilberries at 8 days after treatment ranged from 0.2 to 4.0 ppm. Lichens contained 0.15 to 1.7 ppm. 13 months after treatment. Increasing rate of triclopyr application resulted in increased levels of residues in all cases. Triclopyr was applied once to cowberries at a rate of 0.75 kg/ha in mid-June, July, August or September so that residue level in relation to residence time could be studied. Intervals of 6 to 98 days existed between treatment and harvesting (in late

September). Results showed that residues in cowberries decreased with residence time. Bilberries were similarly treated and harvested in late August. Residues ranged from 0.7 to 0.9 ppm. (intervals of 7 to 69 days) with no relationship between residence time and residue levels. This study suggests that environmental conditions, plant metabolism, and growth stage at time of treatment, as well as species of plant, dictates amount of residue retained in the plant.

The phytotoxic effects of triclopyr result from the disruption of normal phototrophic growth responses (Ghassemi et al., 1981). Although details of its mode of action and metabolism in plants have not been elucidated, this has been an area of active research. Bovey and Meyer (1981) evaluated the phytotoxic effects of triclopyr on monocot and dicot crop seedlings. Many of the species investigated showed morphological symptoms typical of auxin-like herbicides.

Metabolism and Toxicity Studies

Aquatic toxicity

The available toxicological data on triclopyr indicates that there is a wide range of organism response, depending on the test species and on the formulation. Low to moderate toxicity has been observed in the aquatic organisms tested. A summary of aquatic toxicity information, expressed as LC_{50} is presented in Table 2. As can be seen from the data in Table 2, the butoxyethyl ester formulation of triclopyr contained in Garlon 4 is highly toxic to rainbow trout, bluegill, and fingerling fry, with LC_{50} concentrations below 2 ppm. However, Garlon 3A, with the triethylamine salt of triclopyr as the active ingredient, is considerably less toxic, with LC_{50} concentrations for rainbow trout and bluegill reported as greater than 552 and 891, respectively. The pure triethylamine salt itself is more toxic than the Garlon 3A formulation, with toxicities to rainbow trout and bluegill reported as greater than 100 ppm. The contrast in toxicity between the butoxyethyl ester and the triethylamine salt formulations is quite evident in *Daphnia*. Although the test species are different (*Daphnia pulex* for Garlon 4 and *Daphnia magna* for Garlon 3A), some similarity in response within the genera is to be expected, and the observed wide difference in LC_{50} concentrations of 1.2 ppm and greater than 1000 ppm for Garlon 4 and 3A, respectively, indicates probable very real differences in toxicities of these formulations.

Table 2. Toxicity of triclopyr formulations to aquatic organisms.

Formulation	Species	Exposure Time	Temp. (°C)	pH	LC ₅₀ (ppm)	Reference
Garlon 3A	Shrimp	96 hr ¹			895	a
Garlon 3A	Crabs	96 hr ¹			>1000	a
Garlon 3A	Oysters	48 hr ¹			56-87	b
Garlon 3A	<i>Daphnia magna</i>	48 hr ²	19.6-20.3	7.7-8.0	1170	c
Garlon 3A	<i>Daphnia magna</i>	21days ³	19-21	7.8-8.1	1140	c
Triclopyr parent	Rainbow trout	96 hr			117	d
Triclopyr parent	Bluegill	96 hr			148	d
Triclopyr TEA ⁴	Fathead minnow	96 hr	17.0-17.6	7.7-8.2	245	d
Triclopyr TEA ⁴	Fathead minnow	96 hr ⁵			120	d
Triclopyr TEA ⁴	Fathead minnow	192 hr ⁵	24.8-25.8	7.9-8.2	101	d
Triclopyr TEA ⁴	Fathead minnow	96 hr ⁵			114	d
	Ambryo larva stage					
Triclopyr TEA ⁴	Rainbow trout	96 hr	12		>100	e
Triclopyr TEA ⁴	Bluegill	31 days	22		>100	e
Garlon 4	Rainbow trout	96 hr			0.74	b
Garlon 4	Bluegill	96 hr			0.87	b
Garlon 4	Fingerling fry ⁶	96 hr	4.5	7.9	1.4	f
Garlon 4	Fingerling fry ⁶	96 hr	4.5	7.9	1.2	f
Garlon 4	<i>Daphnia pulex</i>	96 hr	21	7.9	1.2	g
Garlon 4	Rainbow fry	96 hr	15	6.2	2.2	g
Garlon 4	Coho fry	96 hr	15	6.2	2.2	g

References:

- a Dow Chemical Company (1981)
- b Dow Chemical Company (1983a)
- c Gresich et al. (1984)
- d Mayes et al. (1984)
- e Johnson and Finley (1980)
- f Servizi et al. (1987)
- g Wan et al. (1987)

Notes:

- 1 Static experiment
- 2 Acute toxicity
- 3 Chronic toxicity
- 4 Triethylamine salt
- 5 Flow through experiment
- 6 Average fish weight = 4.5 g
- 7 Average fish weight = 0.22 g
- 8 Value is given as EC₅₀

Avian toxicity

The available data on the toxicity of triclopyr to birds is limited to a small number of studies conducted by the manufacturer, DOW Chemical Company, which are summarized in Table 3. The acute oral toxicities of both the butoxyethyl ester and triethylamine salt formulations are less than the pure ingredient in the mallard duck (*Anas platyrhynchos*), with LC_{50} concentrations of 1698, 3176, and 4640 mg/kg for triclopyr, Garlon 3A, and Garlon 4, respectively (Weed Science Society of America, 1983). In general, acute and subchronic oral toxicities of triclopyr and its formulations to the birds tested are low.

Mammalian toxicity

A summary of mammalian toxicity studies on triclopyr may be found in Sassman et al. (1984). The available studies (Dow Chemical Company, 1983b and Weed Science Society of America, 1983) indicate slight and moderate acute toxicity, mild subchronic toxicity, and no chronic toxicity utilizing such test organisms as rats, mice, dogs, rabbits, guinea pigs, and monkeys. Triclopyr has no reported adverse effect on reproduction and is not teratogenic in rats or rabbits (Sassman et al. 1984). Residues of triclopyr were not detected in the milk or feces of cows fed a daily grain diet of 22.7 kg/day containing 5 ppm triclopyr for 4 days. Of the total dose of 454.5 mg of triclopyr fed to the cow during the four day test period, 86.4 percent was excreted intact in urine. Triclopyr was not detectable in the urine 24 hours after the feed dosing was stopped (Eckerlin et al., 1987).

Triclopyr was found to exhibit no teratogenic or adverse effects on reproduction, growth, or maturation on three generations of rats in feeding studies utilizing doses of 3, 10, and 30 mg/kg/day (Sassman et al. 1984). Delayed skull ossification was observed in the offspring of pregnant rats administered with 200 mg/kg/day (Hanely et al., 1984 and DOW Chemical Company, 1983a). Triclopyr has not been found to be mutagenic in bacterial assay systems, cytogenetic assays, or mouse dominant lethal studies (DOW Chemical Company, 1983b). In a variety of assay systems, triclopyr was found to be weakly mutagenic in only one test (DOW Chemical Company, 1983b).

Environmental Studies

Limited information is available on the environmental fate of triclopyr in plants,

Table 3. Toxicity of triclopyr in oral exposures to birds. (All LC_{50} values are in mg/kg. Information is from Dow Chemical Company (1983)).

Formulation	Organism	Exposure	LC_{50}
Triclopyr	Mallard duck	Acute ^a	1,698
Garlon 3A	Mallard duck	Acute ^a	3,176
Garlon 4	Mallard duck	Acute ^b	4,640
Triclopyr	Mallard duck	Acute ^b	>5,000
Triclopyr	Bobwhite quail	Subchronic ^b	2,935
Triclopyr	Japanese quail	Subchronic ^b	3,278
Triclopyr (TEA) ^c	Mallard duck	Subchronic ^b	>10,000
Triclopyr (TEA) ^c	Bobwhite quail	Subchronic ^b	11,622
Triclopyr (TEA) ^d	Mallard duck	Subchronic ^b	>10,000
Triclopyr (TEA) ^d	Bobwhite quail	Subchronic ^b	9,026

Notes:

a Exposure time not reported

b Exposure time 8 days

c Triethylamine salt

d Butoxyethy ester

soil and water. Much of the general information has been summarized by Ghassemi et al. (1981) and Sassman et al. (1984). In contrast, many studies have been conducted on the uptake and translocation of triclopyr in plants (see previous sections). These types of studies are important in understanding why triclopyr is an efficient herbicide. However, little work has been done on the metabolic degradation of triclopyr. Limited data are available on the fate of triclopyr in soil. Triclopyr, considered to be a relatively mobile pesticide, is believed to have a short persistence in soil. This is probably due to rapid degradation of the compound by soil microorganisms. Persistence of triclopyr in water is probably of short duration due to rapid photodegradation which is considered the major degradation pathway in the aquatic environment.

Triclopyr in the aquatic environment

Triclopyr may enter the hydrosphere via many pathways including: 1) direct application for pest control, 2) runoff from nonpoint sources, 3) leaching through soil, and 4) aerosol and particulate deposition. In general, pesticides may be removed from the water column by 1) settling of particles to which the pesticide is adsorbed, 2) degradation by microorganisms, 3) uptake by organisms, 4) volatilization, and 5) photochemical decomposition. Triclopyr has been shown to be stable to hydrolysis at pH of 5, 7 and 8, at temperatures of 15°, 25°, and 35°C for 9 months (Hamaker, 1976). Several laboratory studies indicate that photodegradation is the major pathway by which triclopyr is degraded in the aquatic environment. Chemical hydrolysis is not expected to be a major pathway of degradation in the aquatic environment (Ghassemi et al., 1981).

The rate of photodegradation of triclopyr in water is rapid with a half-life ranging from about 2 to 10 hours at 25°C (Weed Science Society of America, 1983; McCall and Gavit, 1986). According to Ghassemi et al., (1981), summarizing product registration data, the major degradation product of triclopyr is 3,5,6-trichloro-2-pyridinol. This compound further degrades to 2-methoxy-3,5,6-trichloropyridine and to other various pyridine polyols (Ghassemi et al., 1981). These products are believed to be further degraded in the aquatic environment to a series of oxidized products such as diketones (Figure 1) (Marshall and Roberts, 1978).

Fate in soil

The fate of pesticides in soil can be described by 6 factors: volatilization, photo-decomposition, adsorption/leaching, runoff, chemical degradation, and microbial deg-

radiation. Because of its low vapor pressure, triclopyr loss via volatilization is expected to be minimal. Photodegradation is probably insignificant in forest systems because of lack of sunlight. In soils, triclopyr is considered to be a relatively mobile pesticide. Adsorption to soil particles is rapid and reversible and is greater in soils with a high organic content. Potential for leaching is determined by the adsorption capacity of a given soil type. Rainfall after field application of triclopyr would lead to some loss of the herbicide due to runoff. Depending on the soil type and climatic conditions, microbial degradation of triclopyr has an average life of 46 days (Worthing, 1983). Degradation by chemical pathways does not occur to any appreciable amount.

Adsorption in soil is a chemical and/or physical process in which substances are collected on the surface of the soil particle. Major factors influencing the adsorption/desorption process on soil particles include soil characteristics and composition, and pesticide characteristics. Triclopyr in the pure form is a picolinic acid herbicide and is anionic (negatively charged). The formulations of triclopyr used in the field are esters and amines and are nonionic compounds. The adsorption reactions of nonionic molecules by soil components are governed by the nature of the substrate being adsorbed, surface properties of the soil, and environmental factors. The adsorption mechanisms for nonionic pesticides are van der Waals forces, ion-dipole and coordination types of interaction, protonation, and hydrogen bonding (Huang, 1980). Environmental factors which affect adsorption/desorption of pesticides are soil pH, temperature, and organic matter content.

Adsorption capacity of a given soil type determines the potential for a herbicide to leach out of the soil. The movement of herbicides through soil involves the interaction of several processes: diffusion and dispersion, mass transfer, leaching and volatilization. Mass transfer involves water as a carrier and movement results from gravity. In general, polar species are more mobile in soils. Among the organic compounds adsorbed in soils increasing mobility occurs in the following order: hydrocarbons < ethers < tertiary amines < nitro compounds < esters < ketones < aldehydes < amides < alcohols < acids (Korte, 1978). Pesticide runoff varies according to the rate of surface water flow and soil types, while leaching depends primarily on adsorption/desorption between the soil constituents and the water percolating through it.

As is apparant, the mobilization of pesticides from the soil into surface runoff is a function of a complex blend of processes. The application rate and the date of application relative to subsequent storm events determine the amount of material available for solubilization. The duration and intensity of precipitation and the soil

moisture content determine the pattern of runoff, that is, the amount which will infiltrate the soil and the amount which will form surface runoff. Vegetation and topography also influence infiltration and runoff. The solubility of the chemical limits the availability of pesticide for leaching into the surface or infiltrating flows. The absorptive capacity of the soil and the vertical distribution of the pesticide in the soil at the time of precipitation determine the amount of material exposed at the soil surface to the runoff where solubilization and mobilization may occur.

Similarly, the degree to which a compound will leach into the vadose zone of the soil horizon, potentially moving into the groundwater, will be governed by the precipitation amount and rate. Interactions with soil, including adsorption and desorption reactions, will affect movement. Other soil characteristics, which influence the infiltration of water in the vadose zone and the contact of water with reactant and adsorbing surfaces, such as void ratios or porosity and soil organic matter content, will affect the vertical distribution and movement of the material.

The solubility of triclopyr in water is relatively high ($K_w = 430$ to 440 ppm at 25°C .), leading to an initial conclusion that the leaching potential of the herbicide is also great. A model simulation of herbicide flow supported the conclusion that triclopyr has a moderately high potential for appearing in runoff (Nutter et al., 1984). The simulation utilized the CREAMS model (Chemicals, Runoff, and Erosion in Agricultural Management Systems) for comparing the expected concentrations of pesticides in runoff from forested watersheds. Field studies using hexazinone showed relatively good agreement between the model predictions and actual runoff concentrations (Nutter et al., 1984). Triclopyr concentrations in runoff were less than those of bromacil and hexazinone, but greater than picloram and dicamba. Triclopyr ranked second out of the five herbicides tested for potential residue appearance in storm flow.

Another measure of the leaching potential of a pesticide is the soil adsorption constant (K_{oc}). K_{oc} is essentially a partitioning coefficient describing the tendency of a chemical to be distributed between the soil and water fractions. Specifically, the soil adsorption constant is defined as the amount of compound adsorbed per unit of soil organic carbon (in $\mu\text{g/g}$, dry basis) divided by the concentration of compound in the water (in $\mu\text{g/ml}$) (Laskowski et al., 1982). This relationship can be expected to reasonably describe adsorption of anionic compounds in which adsorption is a function of the soil organic matter content. The K_{oc} value reported for triclopyr is 27. The soil adsorption constant can be related to a specific soil by the soil adsorption coefficient, K_d , by the following equation (Laskowski et al., 1982), which requires that the organic

matter content of the soil be known:

$$K_{oc} = (K_d \times 10^{-2}) / (\text{Percent organic carbon})$$

Only a few studies on the fate of triclopyr in actual field conditions are available. Molnar et al. (1985) investigated the penetration of triclopyr into the soil. Soil samples were taken from 0 to 20, 20 to 40, and 40 to 60 cm depths on the day of treatment, 4 to 6 weeks and 12 to 14 weeks after treatment. Triclopyr was detectable only in the upper 0-20 cm soil layer and was degraded within three months. Degradation of triclopyr at sites with varying soil and climatic conditions was studied in field and laboratory trials in Sweden (Stark, 1983). In soils with high biological activity both triclopyr acid and ester were decomposed within one year, but in soils with low biological activity the acid and ester could remain for greater than two years. Factors such as organic matter, pH, temperature, and water content influenced the rate of decomposition. Field trials on different soils under barley in Sweden were studied to determine triclopyr residues (Nilsson, 1983). Barley was treated with 960 g-triclopyr/ha at the 2 to 3 leaf stage. Persistence of triclopyr was short and it remained in the 5 to 15 cm soil layer. In eight field experiments in different parts of Sweden, triclopyr triethylamine as Garlon 3A (360 g/liter) at 2.2 kg-active ingredient/ha, and triclopyr butoxyethyl ester as Garlon 4E (480 g/liter) at 1.9 kg-active ingredient/ha were applied to forest soils (Torstensson and Stark, 1982). Triclopyr persisted for at least 1 to 2 years and sometimes longer. Analysis of early spring samplings often contained higher amounts of triclopyr than the previous fall samples. This may have been due to the lower decomposition rate during the winter. This study suggests that persistence under field conditions is related to soil temperature, which in turn points to microbial degradation as a major pathway for disappearance of the compound. Norris et al. (1981, 1987) developed some equations describing the disappearance of triclopyr from soil following applications on some western Oregon pastures. Their results will be compared to the results from the present study and will be discussed more thoroughly in the Results and Discussion section.

Because of the necessities in making some initial predictions regarding the probable environmental fate and behavior of new chemicals, Laskowski et al. (1982) have derived some mathematical equations to describe the environmental behavior of 27 soil-applied chemicals. These equations result in numerical values that are used to express trends in volatilization, leaching, and exposure to biota. The equations, as follows, are utilized as an initial predictor to express the environmental behavior of chemicals on a *relative* basis:

$$\text{Leaching potential} = S/[(V_p)(K_{oc})]$$

$$\text{Leaching index} = [(S)(t_{1/2})]/[(V_p)(K_{oc})]$$

$$\text{Volatility potential} = V_p/[(S)(K_{oc})]$$

$$\text{Volatility index} = [(V_p)(t_{1/2})]/[(S)(K_{oc})]$$

$$\text{On-site exposure} = [(t_{1/2})(K_{oc})(S)(K_{ow})(F)(R)]/V_p$$

$$\text{Off-site exposure} = [(t_{1/2})(V_p)(K_{ow})(V)]/[(K_{oc})(S)]$$

For triclopyr, the following values were used in the equations:

1. Soil degradation half-life at 25°C ($t_{1/2}$): 40 days
2. Vapor pressure in mm Hg at 25°C (V_p): 1.3×10^{-6}
3. Water solubility in ppm at 25°C (S): 430 ppm
4. Soil adsorption constant (K_{oc}): 27
5. Bioconcentration coefficient (K_{ow}): 3

In the equations above, F is the frequency of application, R is the concentration of chemical introduced, V is the volume of material manufactured, and $t_{1/2}$ is the soil degradation half-life at 25°C. The leaching potential (1.2×10^7) and leaching index (4.9×10^8) for triclopyr was high compared to the other pesticides tested. This mathematically supports the conclusions reached in other studies that triclopyr is relatively mobile. The volatility potential (1.1×10^{-10}) and volatility index (4.5×10^{-9}) ranked 23rd out of the 27 pesticides tested. Triclopyr also ranks low for on-site and off-site exposure to soil-applied chemicals.. Laskowski et al. (1982) suggest that by using these mathematical equations the chemical behavior and its effect on the environment can be estimated. The equations may be viewed as a “screening” to predict compounds that may have undesirable environmental characteristics. Adequate field stud-

ies are then required to assess the predicted behavior of the compound.

Chemical and microbial degradation

Relatively little research has been performed on microbial degradation of triclopyr, although microbial degradation is apparently the primary pathway by which triclopyr breaks down. Triclopyr degradation results in the formation of two metabolites; 3,5,6- trichloro -2- pyridinol and trichloro- methoxypyridine (Regoli and Laskowski, 1974). The trichloro- methoxypyridine eventually degrades to CO₂ with 7 to 30 percent evolution of CO₂ at 375 days. McCall et al. (1976) demonstrated the importance of biologic activity in triclopyr breakdown by showing that triclopyr was not degraded in a sterilized soil in which degradation in the same, unsterilized soil was rapid. Chemical hydrolysis of triclopyr in soil is not thought to be a major pathway. It has been suggested that since triclopyr readily photodegrades in water, it may also photodegrade on light-exposed leaves and surfaces (Ghassemi et al, 1981). Further discussion of the environmental fate of triclopyr and its metabolites will be presented in the Results and Discussion section.

MATERIALS AND METHODS

Laboratory Procedures

Residues of triclopyr and metabolites were analysed using gas chromatographic procedures. Extraction and cleanup of samples were performed according to the methodologies developed by Dow Chemical Company personnel, except as noted. All analyses were performed on a Hewlett-Packard Model 5890A Gas Chromatograph using the electron-capture detector. Peak heights and areas were determined with a Hewlett-Packard Model 3392A Integrator. A Megabore (Trademark of J&W Scientific, Inc.) column , Model number, DB5-30M with a film thickness of 1.5 µm was used. Operating conditions for the gas chromatograph are presented in Table 4. Gas chromatograph injections were performed using a 10 µl syringe filled manually to 1µl. Each sample was analysed in triplicate.

Soil samples were analysed by Dow Method ACR 84.2 (McKellar and Brown, 1984) for triclopyr, by Dow Method ACR 77.5 (McKellar, 1977b) for trichloropyrinol and trichloropyridine. Vegetation samples were analysed for all three compounds by Dow Method ACR 77.4 (McKellar, 1977a). Dow ACR 77.5 for trichloropyridinol in

Table 4. Operating parameters for analysis of triclopyr and metabolites on the Hewlett Packard Model 5890 Gas Chromatograph. All temperatures are in degrees Celcius.

	triclopyr	trichloropyridinol	methoxypyridine
Oven temp.	200	160	160
Injection temp	220	220	220
Detector temp.	300	300	300
Carrier gas	Nitrogen with 20 ml/min flow rate		
Column	Megabore capillary column DB5-30M, film thickness 1.5 mm		

soils and Dow ACR 77.4 for trichloropyridinol in vegetation were modified as follows: all reagent and sample volumes were reduced to one-fourth of those described in the methodology. The volume of the acidic alumina column was also reduced.

It should be noted that Tsukioka et al. (1986) have developed a simple and precise microanalytical method for determining the concentrations of triclopyr and its metabolites in natural waters. The stated detection limit for this method is 0.005 ng with a determination limit of 0.00025 $\mu\text{g/ml}$. Triclopyr recovery experiments on river waters were found to be 90-93 with less than 4 coefficients of variation. This method may be applied to the determination of triclopyr residues in other environmental waters.

Field Procedures

Study Area

The field site was located about 10 miles northwest of Bovill, Idaho, (Figure 2) on property owned by the Potlatch Corporation. The site was near Fern Creek, a small

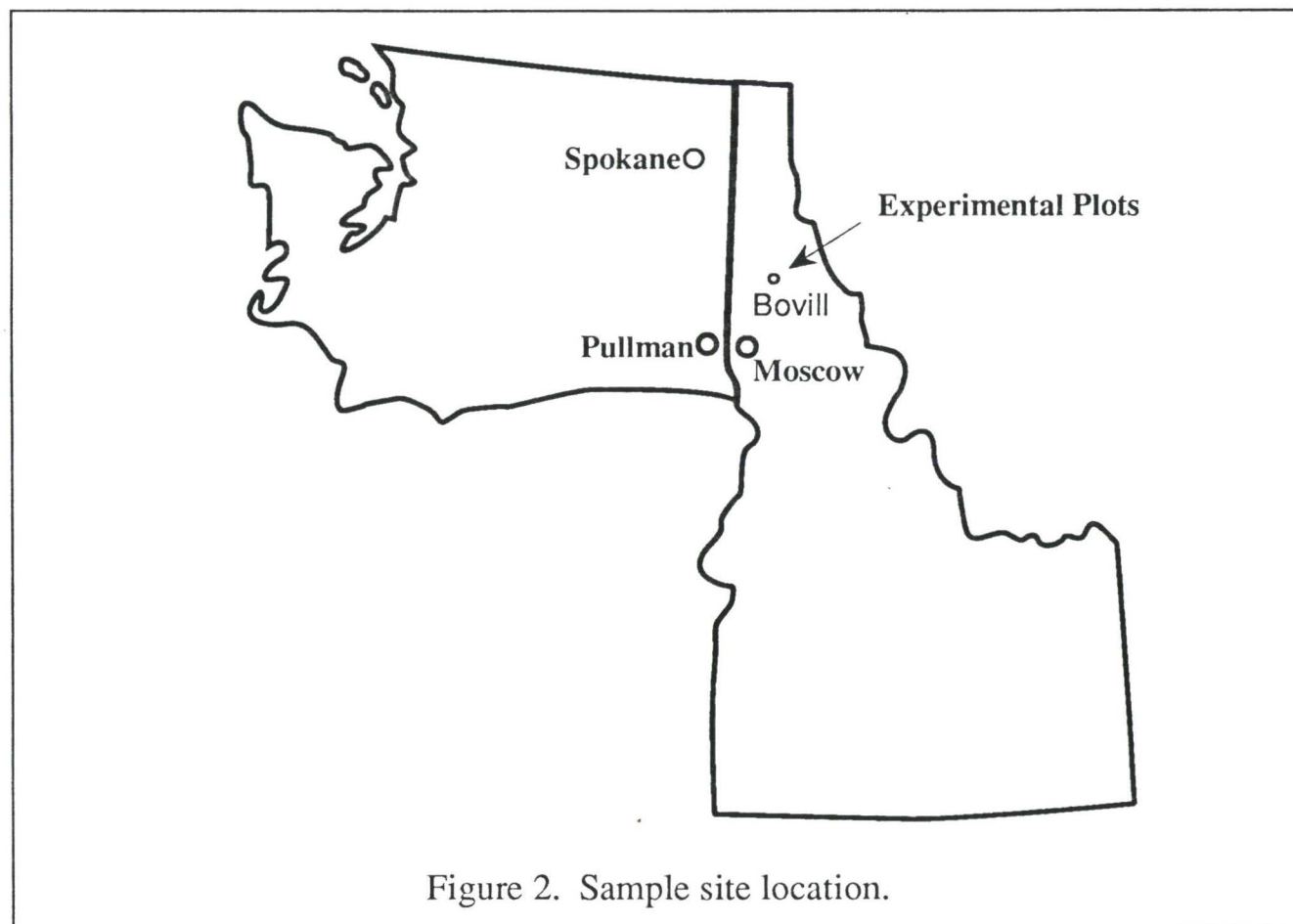


Figure 2. Sample site location.

intermittant tributary of the South Fork of the Palouse River. Soil organic matter ranged from 2% to 18% and averaged 6.5%, and soil moisture ranged from 16% to 37%, averaging 25.8%. Vegetation at the site was composed of such species as horseweed (*Conyza canadensis*), bracken fern (*Pteridium aquilium*), thimble berry (*Rubus parviflorus*), myrtle boxwood (*Pachistima myrsinites*), bull thistle (*Cirsium vulgare*), fireweed (*Epilobium augustifolium*), tall cudweed (*Gnaphalium microcephalum*), and wild hollyhock (*Illiumusa rivularis*), which are typical of forest preparation sites in northern Idaho.

Three 10 m x 10 m square plots were marked at the study site and were designated as North, Middle, and South plots. The plots were located on the eastern side of the west slope above Fern Creek, at about 30 feet of elevation above the creek bed. The slope in the plots was fairly steep, with grades of about 20 to 30%. Lateral distance from the bottom margin of each plot to the creek was about 75 feet.

Herbicide application

Application of herbicide to the test plots was accomplished by ground spraying, using an ultra-low volume spray atomizer, Micron Model Herbi 77. The Micron Herbi employs an atomizer disk and a slow feed rate of about 1 ml/sec to produce a very fine mist of the herbicide mixture, allowing for good control of application. It is believed that reasonably good uniformity of application was achieved in all plots. Garlon 4, obtained from Dow Chemical Company, was mixed with water in a ratio of 3 to 1 (water/herbicide, volume/volume). Application rates were:

	kg/ha	lb/acre
North Plot-	7.2	6.42
Middle Plot-	19.2	17.11
South Plot-	9.6	8.55

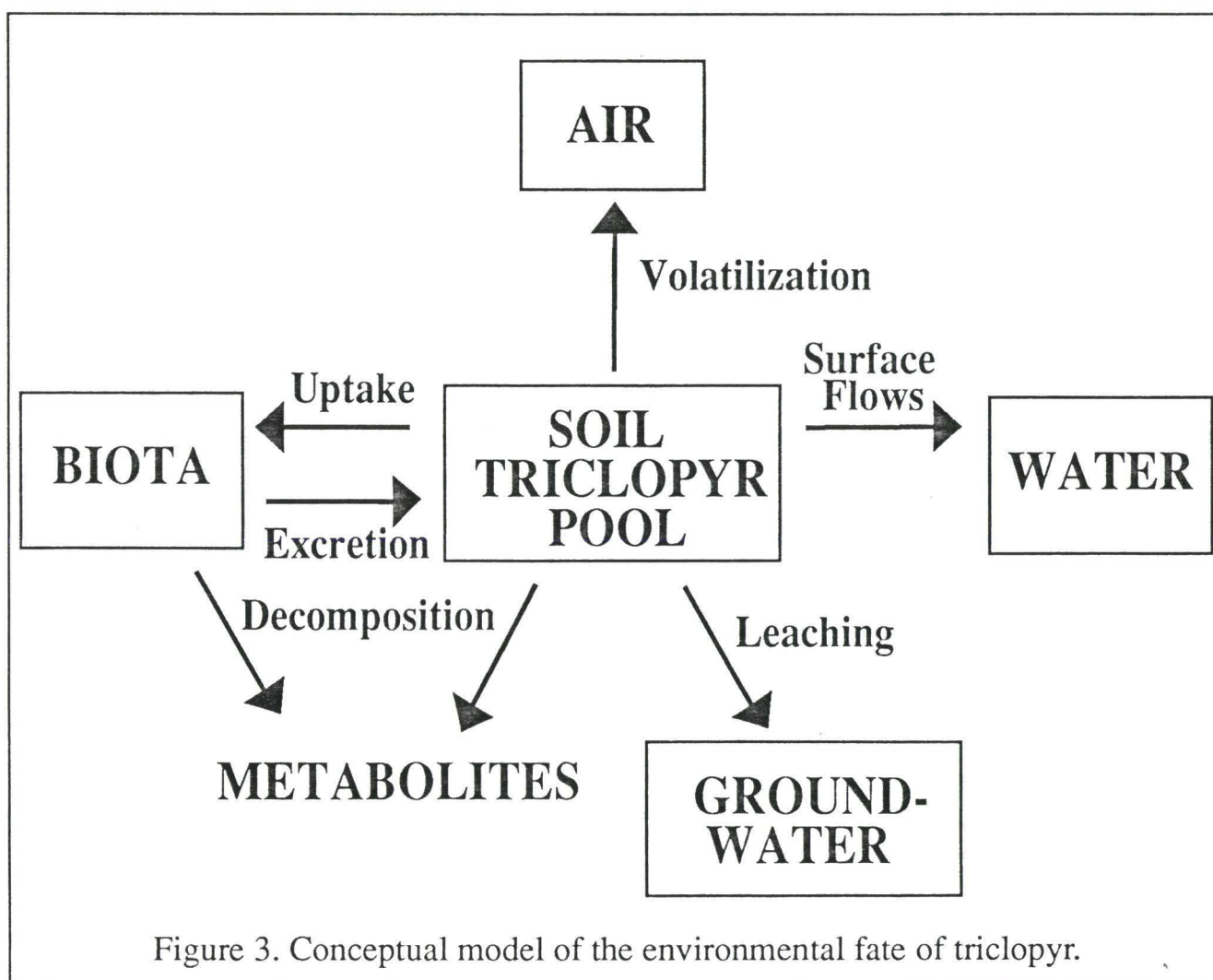
Sampling and storage

Soil was collected from the top 2-cm layer at sampling points above, below, and within the plots prior to, and 2, 7, 14, 180, 225, and 700 days following herbicide application. Vegetation samples were also collected at the same points and times. Soil profile samples were taken using a manual 10 cm diameter hand soil auger. The resulting cores were partitioned into 10 cm soil increments to a depth of 50 cm. All samples were iced and stored in the dark for transport to the laboratory. At the

laboratory, soil and vegetation samples were ground in a Wiley Mill until the material would pass a 2 mm Standard U.S. sieve. The samples were stored at -18°C until analysis.

RESULTS AND DISCUSSION

As stated in the introduction, the general goal of the study was to provide information for determining the likely exposure of non-target organisms to triclopyr and its metabolites (i.e., for a risk assessment). This requires that a reasonable appreciation of the patterns of concentration of the chemical that result with time following applications be determined. Figure 3 presents a conceptual model of the movement of triclopyr in the environment. In the model, the environment is broken into compartments so that an evaluation of the processes that govern interactions between the compart-



ments may be isolated and more easily understood and quantified. The model is, of course, a simplification, particularly in regards to the biotic components. Separate biotic components for each of the air, soil, and water compartments could also be represented in the figure but were excluded, as the figure is primarily addressing environmental movement, not exposure. The persistence of triclopyr in soils and vegetation and the pathways of movement of the chemical to and from the initial point of application (i.e., soils and vegetation) will be discussed in this section. Data gained from the present study will be presented and placed in perspective in terms of data from previous studies and from other herbicides.

Volatilization

Volatilization is one of the processes by which pesticides may be mobilized from the soil compartment. Volatility is controlled by the many variables which govern the movement of the chemical to and from the site of evaporation and the rate of evaporation of the chemical. An initial evaluation of the importance of volatility in removing pesticides from the soil may be made by examining the vapor pressure (McCall and Swann, 1978). The vapor pressure of triclopyr is relatively low, 1.3×10^{-6} mm Hg (168 μ Pa) at 25°C. Laskowski et al. (1982) ranked the volatility potential of triclopyr at 23rd out of a group of 27 pesticides analysed. Triclopyr volatility potential, as defined by the authors, was 4 orders of magnitude less than some of the pesticides with the greatest volatility potential, such as heptachlor, lindane, and nitrapyrin.

Swann et al. (1979) have presented an expression which relates volatility to both the water solubility in ppm (K_w) and the soil adsorption constant (K_{oc} , see later discussion), as well as to the vapor pressure (in mm Hg). These researchers obtained good correlation between measured soil volatility rates of 9 pesticides and an expression containing these variables. They presented the following equation for determining the half-life ($t_{1/2}$) of a chemical in soil when losses due to volatility alone are considered:

$$t_{1/2} = [1.58 \times 10^{-8}(K_{oc})(S)]/V_p$$

Using this expression for triclopyr, a half-life of about 141 days is obtained, again indicating that volatilization is likely to be a relatively minor component of removal of triclopyr from soils. Figure 4 shows a plot of the projected volatilization of triclopyr from soil at 25°C. The plot was calculated from the equation above. Actual removal due to volatilization should be expected to proceed at slower rates, as lower temperatures may be expected for much of the year. The average daily temperatures during

Figure 4. Calculated plot of triclopyr volatilization at 25°C. (See text for details.)

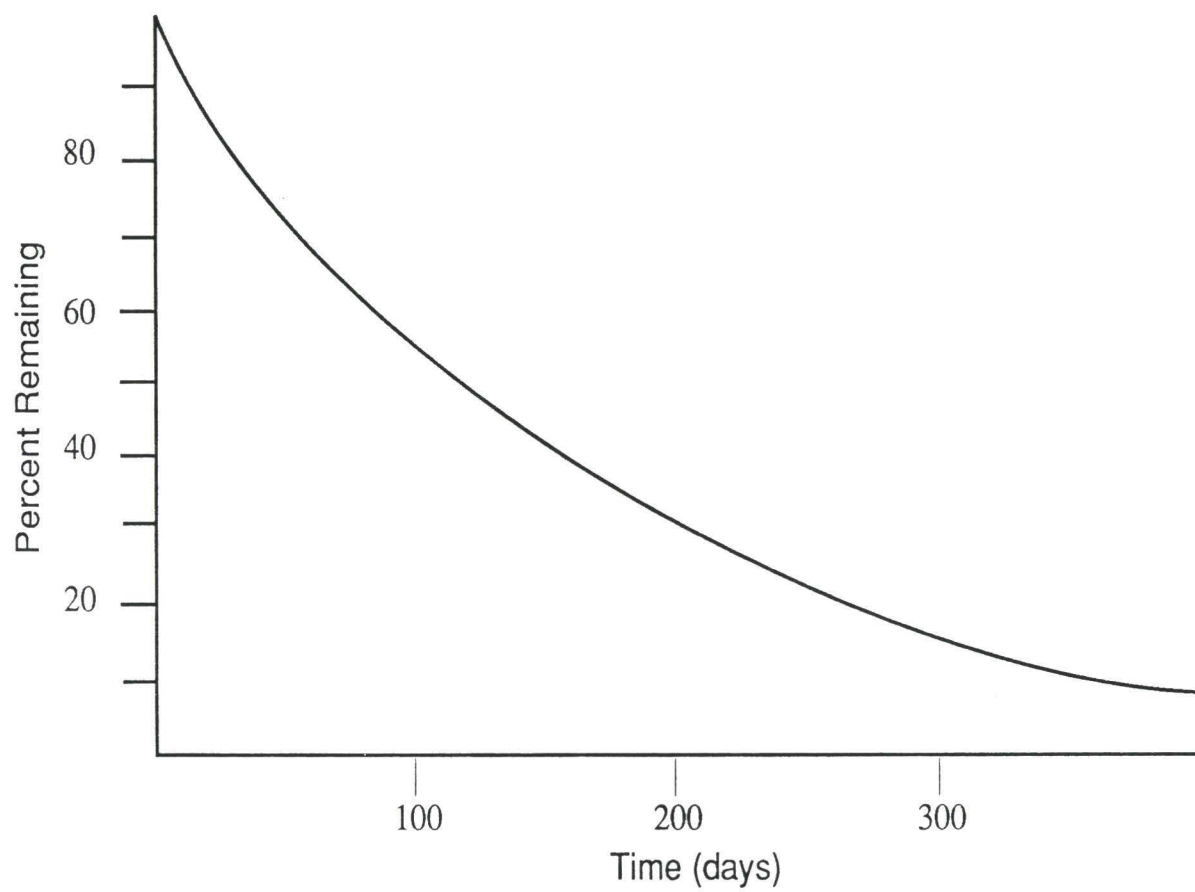
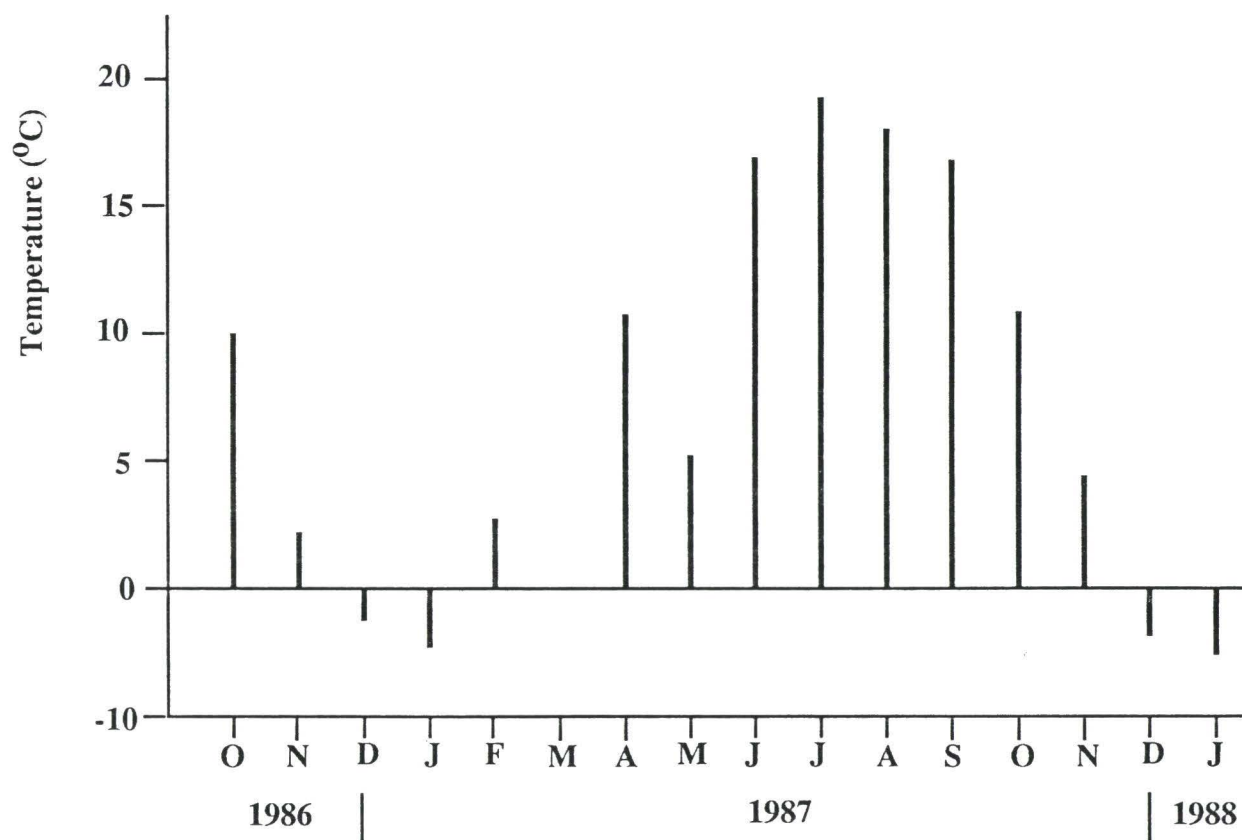


Figure 5. Average daily temperatures in vicinity of experimental plots during study period. (Temperatures are averaged from daily average temperatures at three northern Idaho observation stations near to site.)



the study period averaged from daily temperature averages from three northern Idaho observation stations near the application site are graphed in Figure 5.

Persistence in Soils

Persistence of pesticides in soils is a function of the rate of application, volatilization, leaching, hydrolysis and photolytic decomposition, vegetative uptake, and microbial degradation. Expressions describing the behavior of triclopyr and its primary metabolites in the soil were derived from data obtained during the study described here. Figures 6 to 8 present plots of the measured soil concentrations of triclopyr and metabolites following the experimental applications. The data from which these plots were constructed are given in Tables A-1 to A-3 in the Appendix.

The disappearance curves for triclopyr and the pyridine product in the soil, as observed in this study, are bimodal and each curve can be described by two first-order equations:

for triclopyr, time 0 to 16 days-

$$C_t/C_i = 0.767 - 0.03t$$

for triclopyr, after 16 days-

$$C_t/C_i = 0.312 - (1.46 \times 10^{-3})t$$

for trichloromethoxypyridine, time 0 to 11 days-

$$C_t/C_i = 0.626 - 0.025t$$

for trichloromethoxypyridine, after 11 days-

$$C_t/C_i = 0.372 - (1.36 \times 10^{-3})t$$

In the above equations, C_i is the initial concentration of the compound, and C_t is the concentration at time, t . Half-lives of triclopyr and the pyridine metabolite ranged from about 9 to 130 days and about 5 to 94 days, respectively, using the equations above. These values are consistent with half-lives of triclopyr in soils and other media, as determined in previous studies (Table 5).

The shape of the observed curves may give some insight into the processes which are determining the amount of materials remaining in the soil. As discussed previously

Table 5. Half-lives of triclopyr in soils and water. (Half-lives are in days, unless otherwise noted.)

Medium	Condition	Half-Life	Reference
Silty clay loam soil	Laboratory 35°C.	10	Dow Chemical Co. (1983b)
Loam soil	Laboratory 35°C.	46	Dow Chemical Co. (1983a)
Soil _a	Field	14-16	McKellar et al. (1982)
Soil _a	Not reported	40	Laskowski et al. (1982)
Etelka silty clay loam	Field 1-2 % organic matter	75	Norris et al. (1987)
Whobrei silty clay loam	Field 2-5 % organic matter	81	Norris et al. (1987)
Yolo County loam	Laboratory 0.8 % organic matter, pH 6.5, 35°C.	45	Hamaker and Goring (1976)
Flanagan silty clay loam	Laboratory 4.2 % organic matter, pH 5.8, 35°C.	12	Hamaker and Goring (1976)
Water	Laboratory pH 5, 35°C.	2.1 hr	McCall and Gavit (1986)
Water	Laboratory pH 5, 35°C.	12.2 hr	McCall and Gavit (1986)
Water	Laboratory 25°C.	10 hr	Weed Science Soc. Amer. (1983)

(a) Cited in McCall and Gavit (1986).

(b) Type of soil not reported.

(c) Half-life of triclopyr acid form in water.

(d) Half-life of triclopyr ester form in water.

Figure 6. Disappearance of 3,5,6-trichloro-2-pyridinyloxyacetic acid (triclopyr) in soils following ground application. (Concentration values are expressed as concentration at time = t (C_t), divided by the initial concentration (C_i). Values are averages for all plots.)

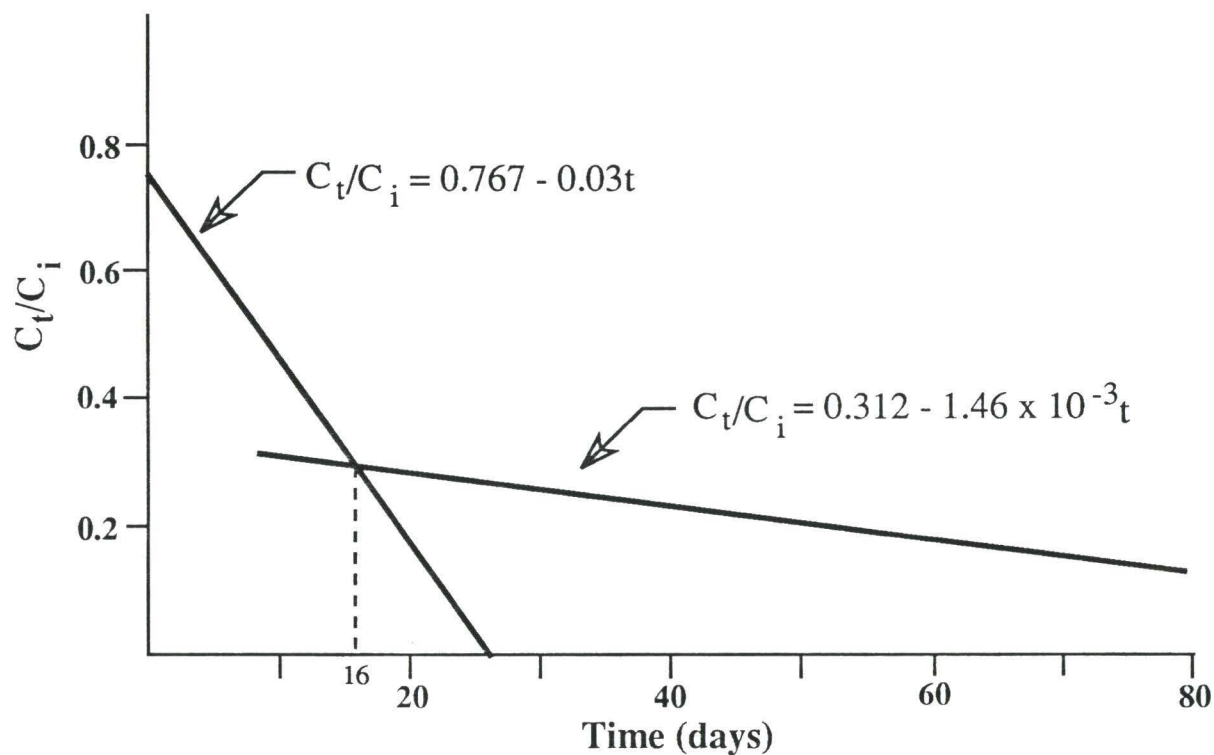


Figure 7. Disappearance of 3,5,6-trichloro-2-methoxypyridine in soils following ground application. (Concentration values are expressed as concentration at time = t (C_t), divided by the initial concentration (C_i). Values are averages for all plots.)

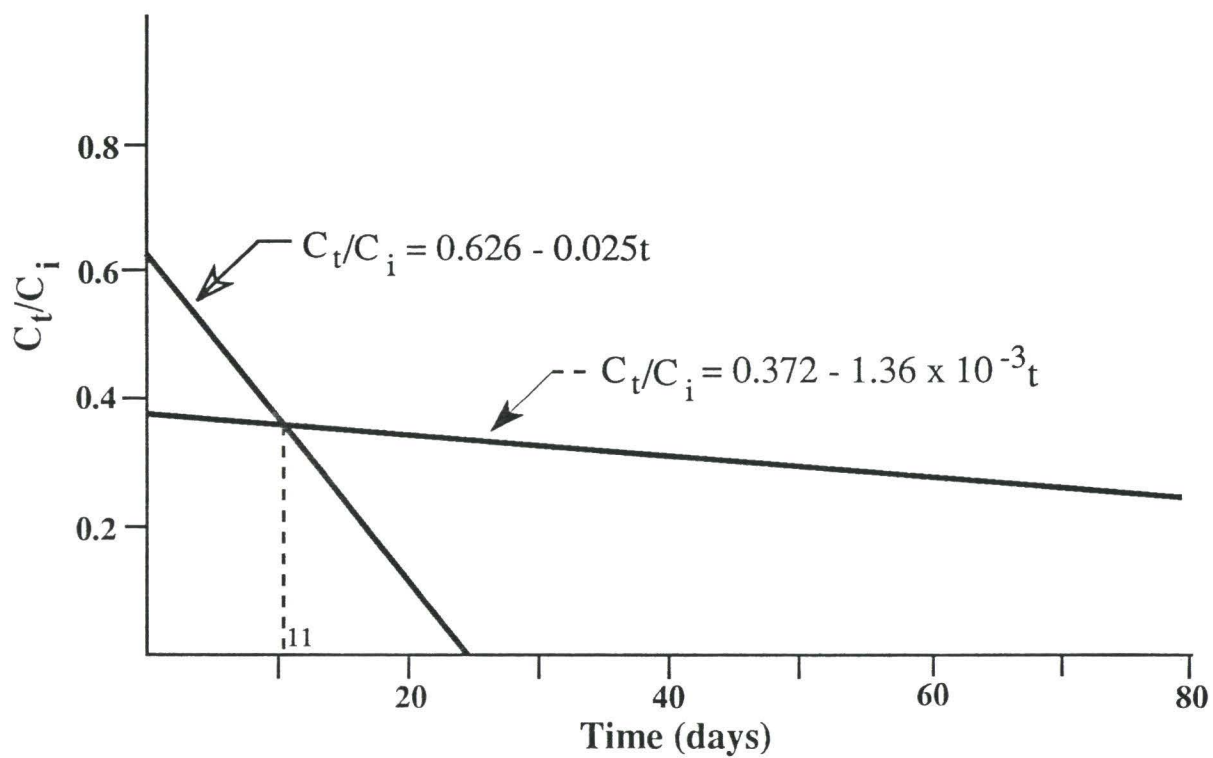


Figure 8. Disappearance of 3,5,6-trichloro-2-pyridinol in soils following ground application. (Concentration values are expressed as concentration at time = t (C_t), divided by the initial concentration (C_i). M, S, and N are plot designations.)

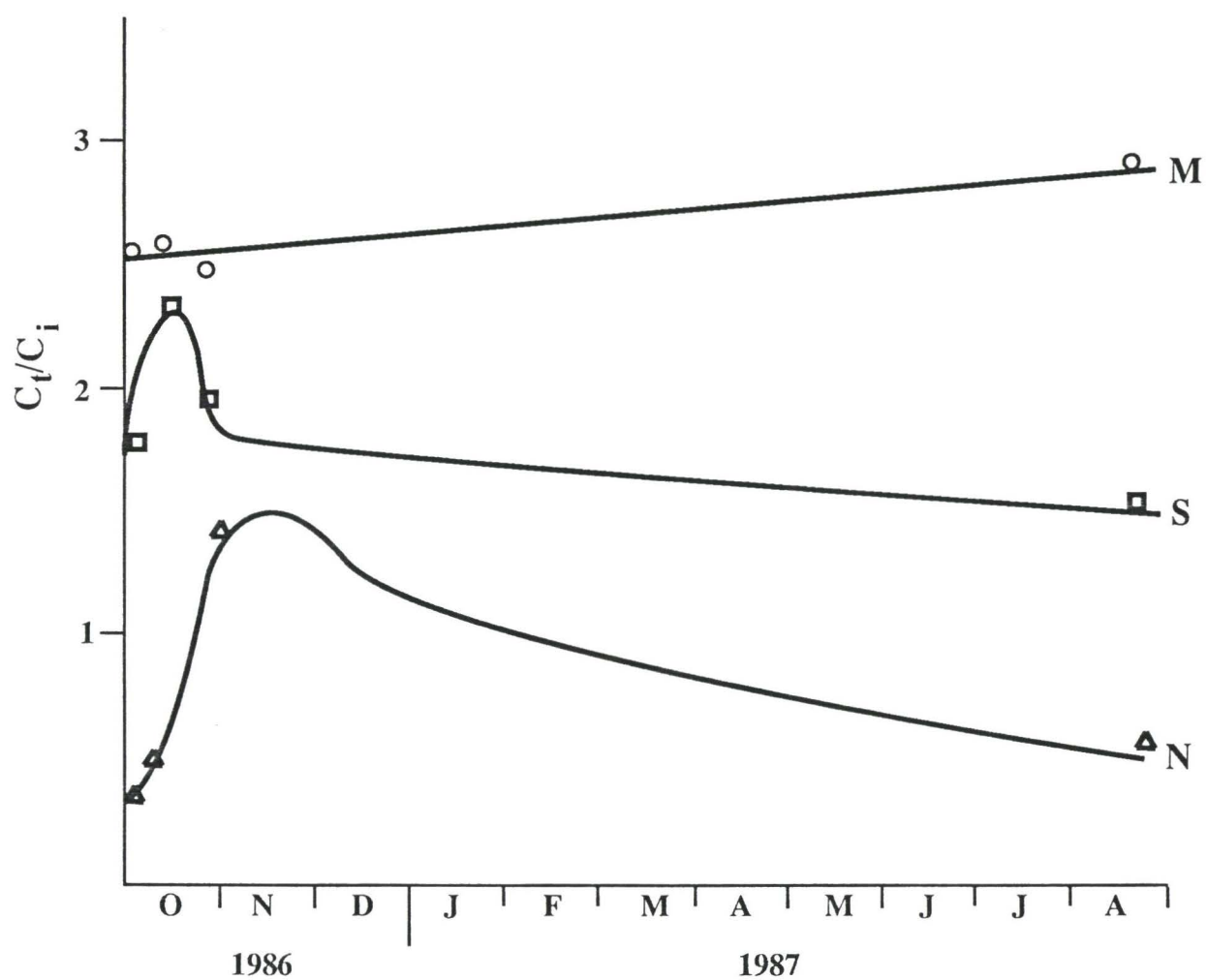
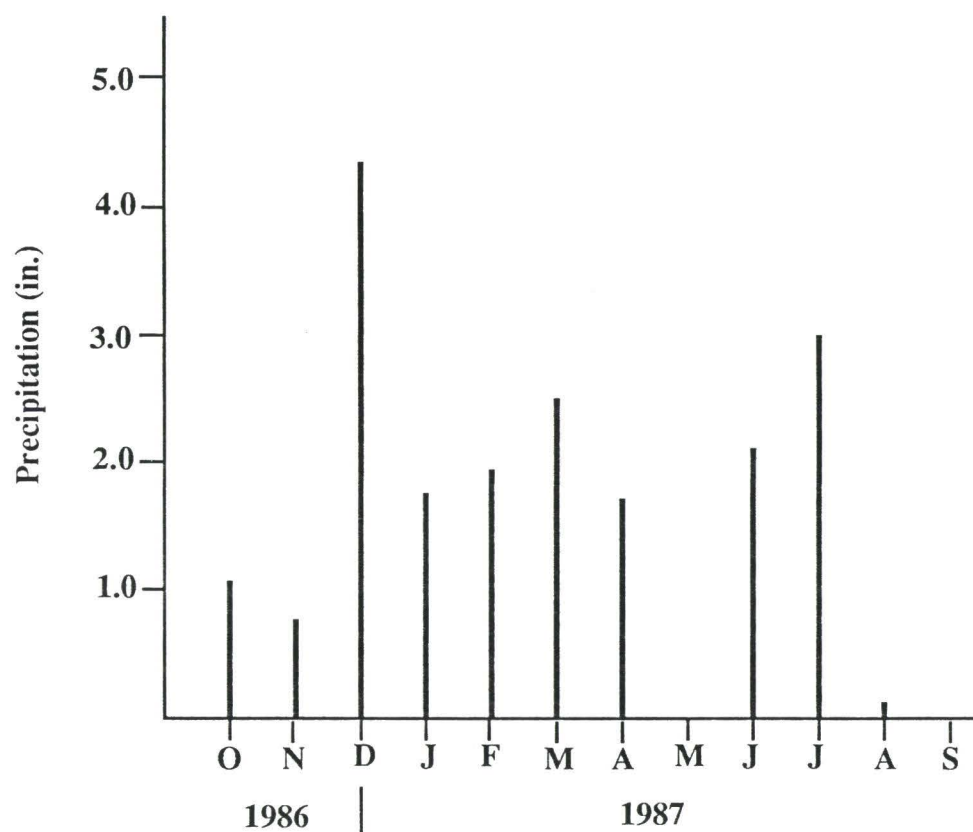


Figure 9. Average monthly precipitation measured during the study period at three north Idaho stations near the experimental site. (Values graphed are averages of the three station observations.)



volatization is expected to play a minor role in removal of triclopyr from the soil. Comparison of Figures 6 and 7 emphasizes this observation. Leaching of material could be important in removing both triclopyr and metabolites from the soil and will be discussed in the context of the soil profile samples. Photodegradation, especially during the dry, cloudless periods which followed the applications, could be important in breaking down triclopyr on the exposed soil and vegetation surfaces (Figure 9 shows the average precipitation measured during the study period at three north Idaho stations located near the experimental site). It is expected that the appearance of breakdown products would show initial increases, corresponding with the disappearance of the parent compound, with photolytic decomposition of triclopyr. This was observed for both the pyridinol and pyridine compounds (Figures 7 and 8).

The trichloropyridinol metabolite showed initial increases with subsequent declines in soil concentrations in the two test plots with the lower application rates (South and North Plots), but showed increasing concentrations in the Middle plot with the highest application rate (Figure 8). The observed patterns may reflect not only the conversion of the triclopyr to breakdown products, but also vegetative uptake and subsequent leaching of materials from vegetation into the soils. Although the relative contributions of these processes (breakdown vs. leaching from vegetation into soils) cannot be determined from the available information, comparison of the plots of triclopyr and the pyridinol and pyridine products shows that, unlike the other two compounds, pyridinol accumulated in the test plots, particularly in the South and Middle plots.

Photolytic decomposition of triclopyr on the soil and vegetation surfaces could account for the shape of the disappearance curves for both triclopyr and its metabolites. However, the shape of these curves do correspond with observations of typical patterns of microbial degradation of other pesticides. Microbial decomposition of pesticides is often a co-metabolic process, as the pesticides commonly are poor energy sources (Goring et al., 1975). In addition, migration of the pesticide into and out the soil matrix (adsorption and desorption) may be occurring constantly, so that the microbial utilization becomes flux-limited rather than concentration limited. Flux-limitation is especially common at lower concentrations, and as a result, rates of degradatory processes may shift from concentration-limitation to flux-limitation with time. For example, it was found that the disappearance of picloram, when plotted on semi-log paper, was described by a straight line at high concentrations but displayed a curve with decreasing slope at lower concentrations (Laskowski et al., 1982). The results from this study, when plotted on semilog graphs, Figures 10 to 11, also display

Figure 10. Semi-log plot of disappearance of 3,5,6-trichloro-2-pyridinyloxyacetic acid (triclopyr) in soils following ground application. (Concentration values are expressed as concentration at time = t (C_t), divided by the initial concentration (C_i). Values are averages for all plots.)

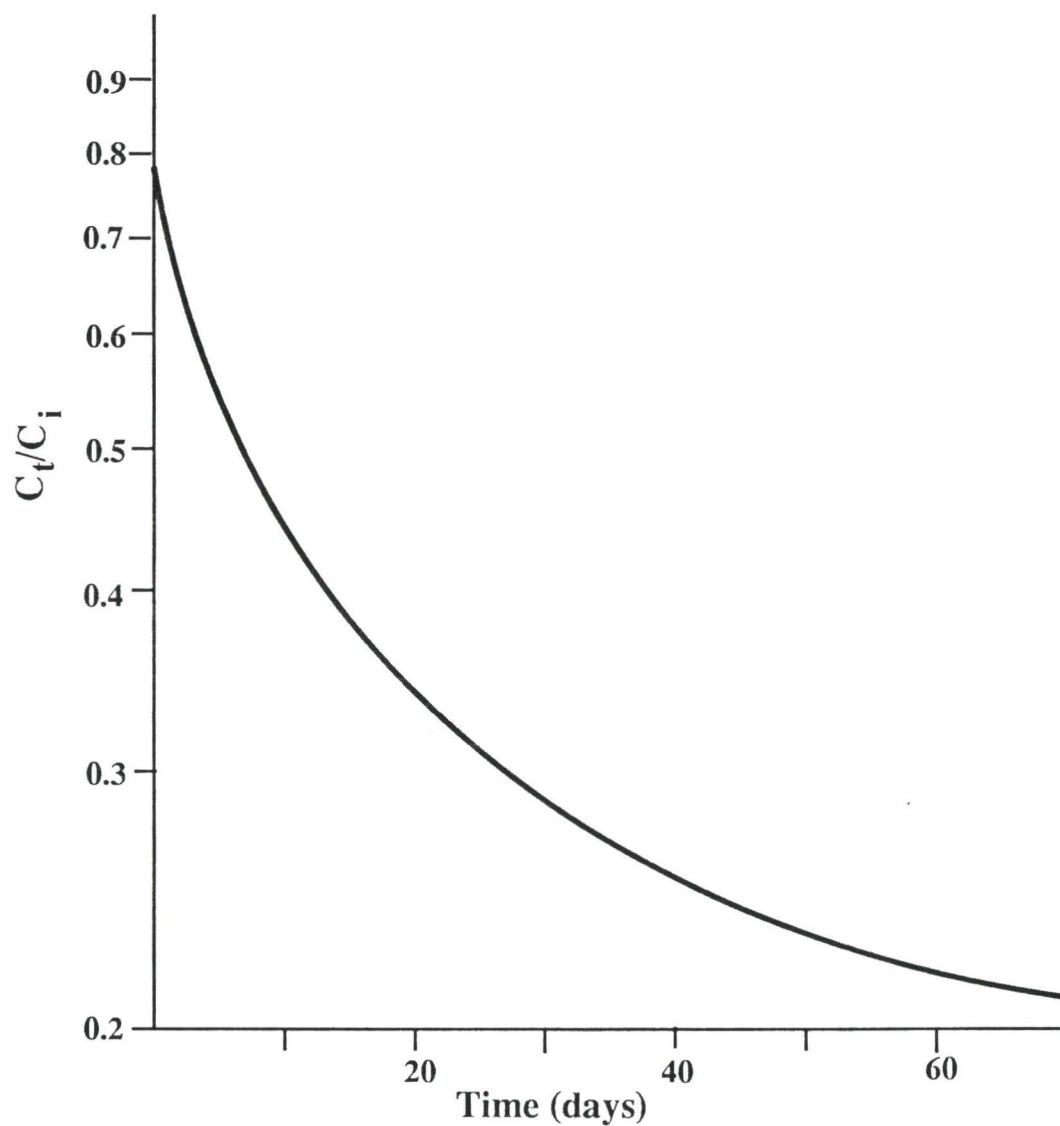
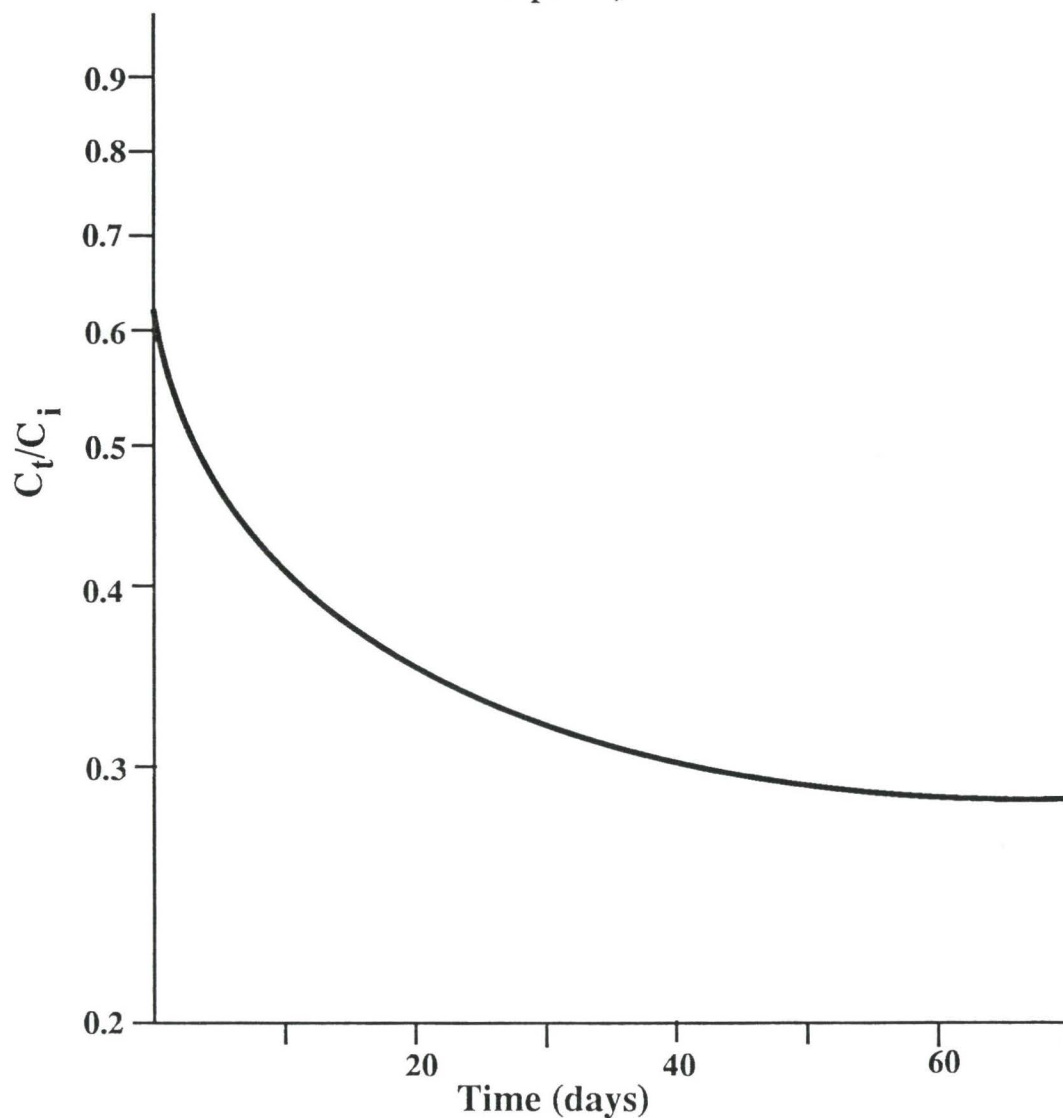


Figure 11. Semi-log plot of disappearance of 3,5,6-trichloro-2-methoxypyridine in soils following ground application. (Concentration values are expressed as concentration at time = t (C_t), divided by the initial concentration (C_i). Values are averages for all plots.)



the decreasing slope, indicating possible flux limitation of degradation of triclopyr in soil. When degradation of the compound is flux-limited, soil organic matter composition can be expected to strongly contribute to the actual observed rates of disappearance as the soil organic matter often dominates the soil absorption processes.

Regoli and Laskowski (1974, as cited in Ghassemi et al., 1981) report that triclopyr degrades first to pyridinol and then to pyridine. The plots of accumulation and disappearance of triclopyr and metabolites which we observed seem to confirm this degradational sequence. The accumulation of pyridinol in the soil warrants further examination. The pattern of accumulation observed in the plots suggests not only that pyridinol is being formed by breakdown of triclopyr, but also that the pyridinol itself is more resistant to breakdown and to removal by other processes. Accumulation of pyridinol seems to be very dependent on the initial rate of triclopyr application. In the Middle plot (19.2 kg/ha application rate), pyridinol concentrations at the end of the study period were about 2.5 times the initial concentrations detected immediately following herbicide application. In both the North and South plots (7.2 and 9.6 kg/ha, respectively), pyridinol concentrations increased rapidly during the first few months following herbicide application, then declined to lower levels at the end of the study period. Even in the North plot, which had the lowest rate of triclopyr application, pyridinol concentrations at the end of the study were above those immediately detected after the application. According to Marshall and Roberts (1978) the conversion of pyridine to pyridinol is a reversible process in soils, and the relative accumulation of pyridinol may result from the reconversion of the pyridine product.

Another possible explanation for the lower concentrations of pyridine in the soil is its higher solubility in water. Mobilization of pyridine from the soil matrix in runoff and groundwater flow would reduce the remaining soil concentrations. However, the results of pyridine analyses in the soil profile samples, as will be discussed later, are not consistent with groundwater mobilization of pyridine, although runoff mobilization can possibly be a factor in the results.

These observations are similar to results obtained with other soil types, and with predictions from the laboratory studies, as discussed in the literature review (Table 6). The soil adsorption coefficient, K_{oc} , of pyridinol for 3 soils ranged from 114 to 156, indicating relatively strong affinity for adsorption onto soils, with concurrent reduction in leaching potential (Hamaker, 1974). In comparison, the reported range of K_{oc} values for triclopyr in 12 soils in a similar study ranged from 12 to 78 (Hamaker, 1975). McKellar (1977c) reported that trichloropyridinol residues in 6 soils reached a

Table 6. Adsorption properties of triclopyr and trichloropyridinol in soil.

Formulation	Adsorption Parameter	Content (%)	Organic Value	Coefficient	Reference
Triclopyr TEA	K_d	0.081-21.7	0.016-14.5		Hamaker (1975)
Triclopyr TEA	K_{oc}	0.081-21.7	12-78		Hamaker (1975)
Trichloropyridinol	K_d	0.081-21.7	0.63-5.64		Hamaker (1974)
Trichloropyridinol	K_{oc}	0.081-21.7	114-156		Hamaker (1974)
Triclopyr BEE	K_{oc}	NR	6000		McCall et al. (1983) ¹
Triclopyr TEA	K_{oc}	NR	27		Laskowski et al. (1982) ¹
Triclopyr TEA	K_{oc}	NR	27		Kenaga (1980)
Trichloropyridinol	K_{oc}	NR	130		Kenaga (1980)

Notes: NR = Not reported.

(1) Cited in McCall and Gavit (1986).

peak between 28 and 56 days following triclopyr application, declining after that time.

The soil profile samples, taken 648 days following triclopyr application, give some insight into the vertical migration of herbicide and its breakdown products in the soil vadose zone. Results of the soil profile analyses are given in Tables A-4 to A-6 in the Appendix, and are displayed graphically in Figures 12 to 14.

The highest residues of triclopyr were found in the Middle plot on the surface samples. However, the results from the surface samples are difficult to interpret, as the two profile samples taken from the upper 2 cm contained 0.994 and 53.335 ppm, respectively, for an average triclopyr soil concentration of over 27 ppm. This wide range probably represents spacial heterogeneity in the initial application of the herbicide. Even excluding the high values in the surface samples from the Middle plot, the average concentrations in the North and South plots were about 6 times lower than Middle plot average triclopyr concentrations. It should be noted that in Figure 12 the abscissa for the Middle plot (B) is different than for the other plots. The application rate in the Middle plot was only about twice as great as in the others, and the enhanced persistence of triclopyr in the Middle plot would suggest that perhaps concentration, rather than flux rates, limit the rate of triclopyr degradation at the higher concentrations.

The graphs of triclopyr in the soil profile show that the compound appears to be mobile in the upper vadose zone, as would be expected from the solubility product. Triclopyr was relatively evenly distributed in the top 40 cm of soil in all of the plots, unlike the breakdown products, which were more concentrated in the upper 2 cm in most of the plots. Unfortunately, the soil auger available for this study yielded intact core from the upper 40 cm, so observations of deeper soil layers could not be made. However, a reasonable interpretation of the figures would indicate that triclopyr is more mobile in the soil horizon than the breakdown products.

The maximum concentration of the pyridinol product detected in the soil after 648 days following application was 2.429 ppm, with an average concentration of 0.441 ppm in all plots. The highest average concentrations of pyridinol were detected in the Middle plot where the highest triclopyr applications were made. Results for the pyridine product were similar, with highest average soil profile concentrations in the Middle plot. The maximum concentration of pyridine detected in the soil profile samples was 0.121 ppm, and the average soil profile concentration was 0.041, about an order of magnitude lower than the pyridinol concentrations.

Figure 12. Concentrations of 3,5,6-trichloro-2-pyridinyloxyacetic acid (triclopyr) in soil profile samples taken from North (A), Middle (B), and South (C) plots 648 days following triclopyr applications. (Note different abscissa scales.)

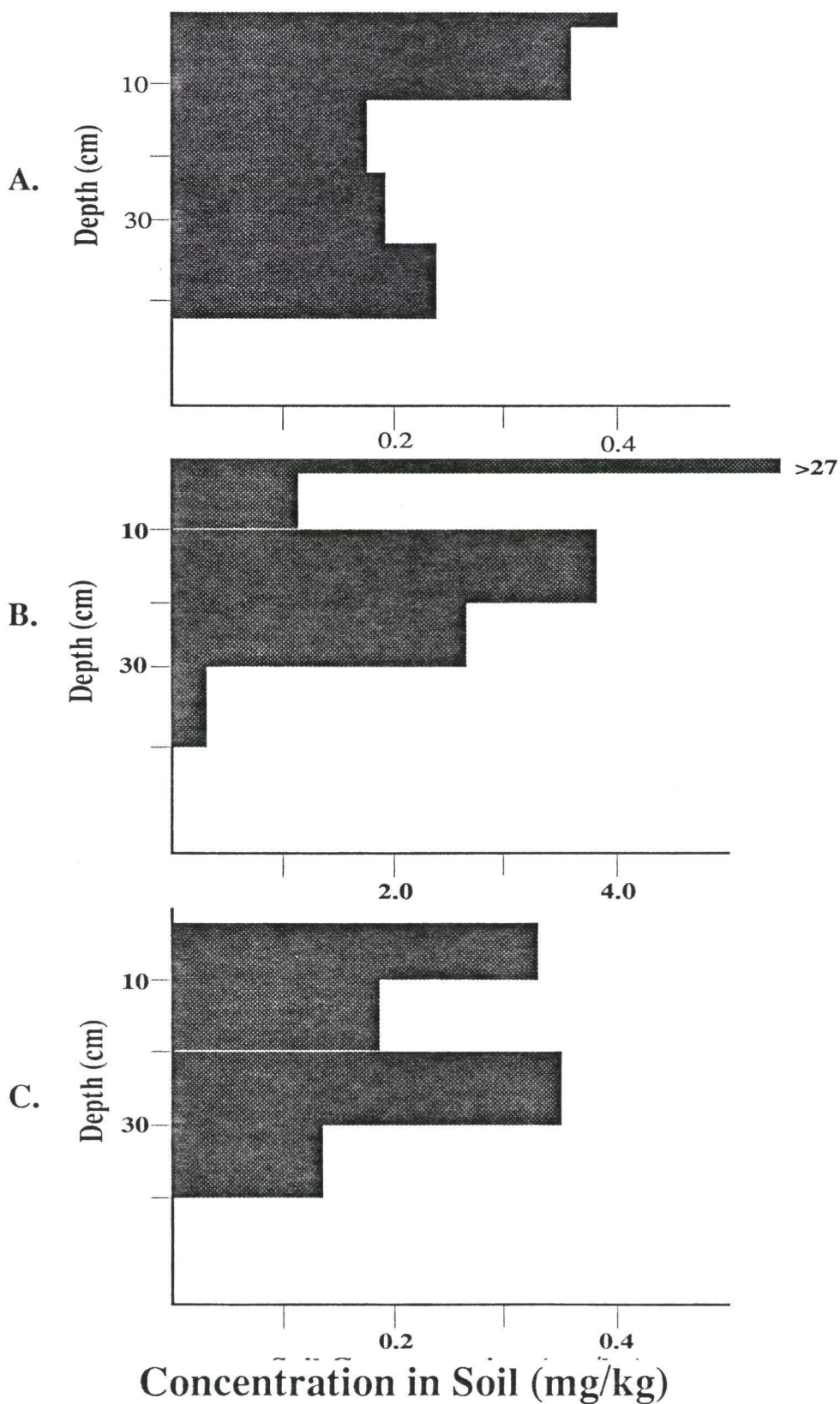


Figure 13. Concentrations of 3,5,6-trichloro-2-pyridinol in soil profile samples taken from North (A), Middle (B), and South (C) plots 648 days following triclopyr applications.

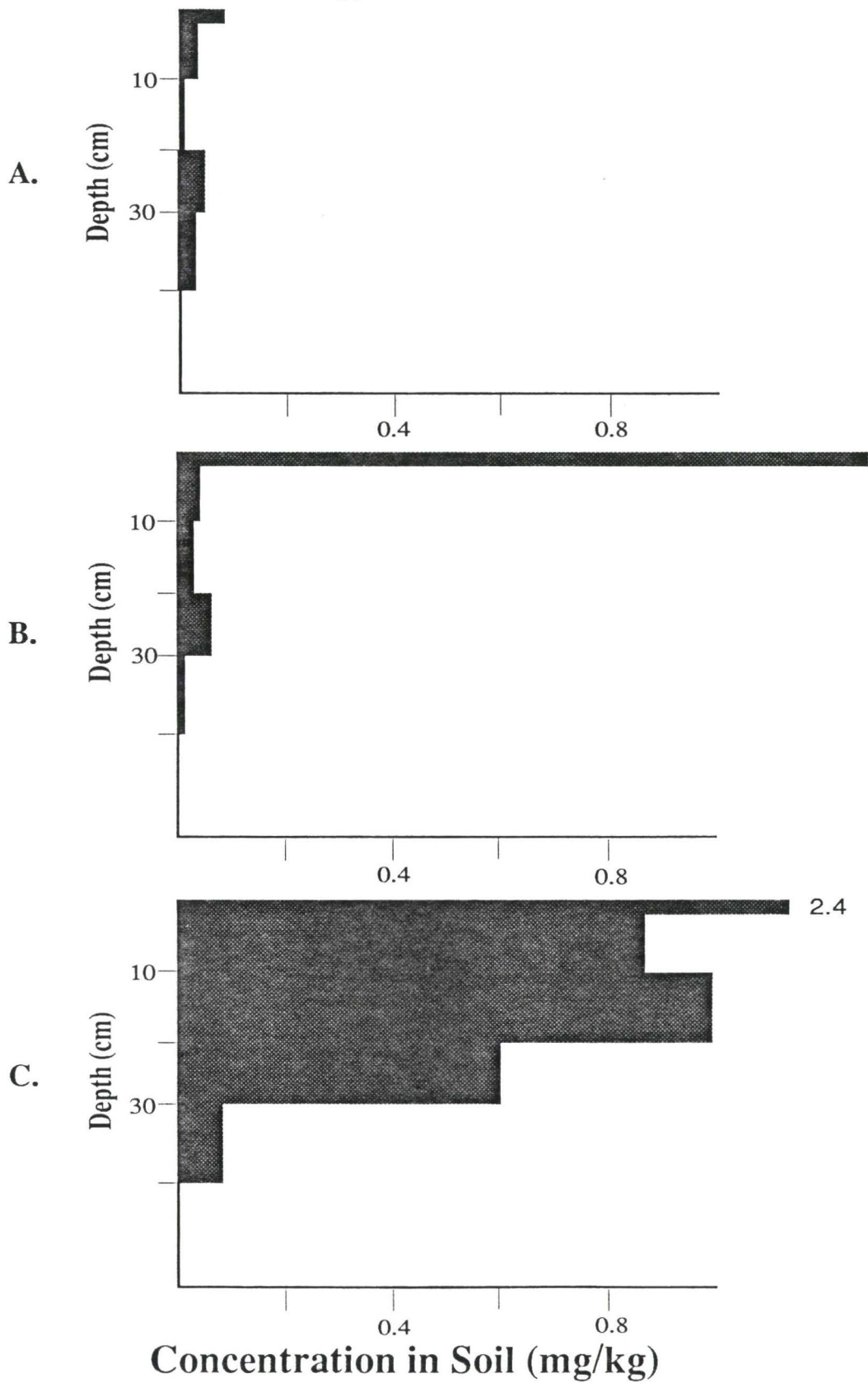
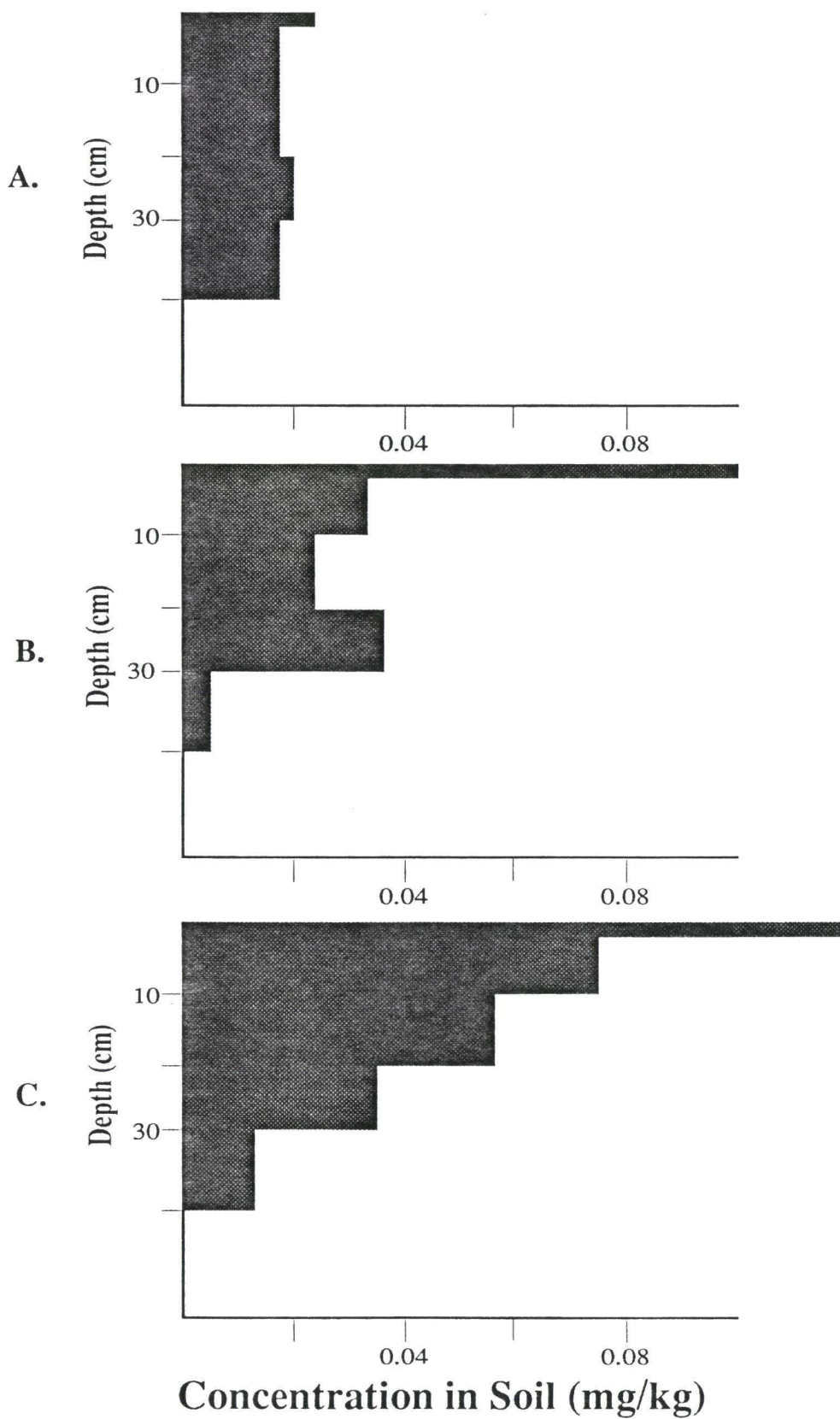


Figure 14. Concentrations of 3,5,6-trichloro-2-methoxypyridine in soil profile samples taken from North (A), Middle (B), and South (C) plots 648 days following triclopyr applications.



Results of the vegetation analyses are given in Tables A7 to A9 in the Appendix, and in Figures 15 to 17, expressed as C_t/C_i . The patterns of triclopyr and breakdown product concentrations shown in Figures 15 to 17 in the vegetation are interestingly similar. Most of the vegetation sample series for each plot demonstrate increased concentrations above the initial values, followed by relatively step declines. The most likely processes controlling this pattern are initial uptake of triclopyr with subsequent metabolic breakdown in the plant tissues into pyridinol and pyridine. The peaks of the metabolites lag behind the triclopyr peaks. As the plants die and decay, both from the action of the herbicide and from natural processes, the compounds may leach into the soil. These vegetation results are consistent with the soil observations and indeed may be partially contributory to the patterns of triclopyr and breakdown products in the soil.

CONCLUSIONS AND RECOMMENDATIONS

Following application, triclopyr degraded relatively rapidly in the northern Idaho soils present in this study. The degradation of triclopyr appears to involve first the formation of the 3,5,6- trichloro -2- methoxypyridinol product, with subsequent formation of 3,5,6- trichloro -2- methoxypyridine. Using the equations determined in this study, triclopyr levels in soils after about 213 days should be 3 orders of magnitude less than initial concentrations. The pyridine product can be predicted to appear rapidly following triclopyr application, then subsequently degrade also at a rapid rate. Pyridine concentrations in soil can be expected to be 3 orders of magnitude less than the early peak concentrations in about 273 days, using the equations from this study. The patterns and lifetimes of persistence for triclopyr and its breakdown products observed in the present study on northern Idaho soils agree with those predicted from laboratory studies and with data from other field studies.

The trichloropyridinol metabolite is less mobile and appears to decompose slower than triclopyr and pyridine. Pyridinol may be expected to accumulate in soils, at least for short periods of time, following triclopyr applications. At the application rates used in the North and South plots, pyridinol levels in the soil declined after first reaching a peak within a few months after triclopyr application. The results for the pyridinol breakdown product were more variable than for triclopyr and the pyridine product and did not lend themselves to mathematical description. Pyridinol concentrations in the soil profile samples, taken 648 days following triclopyr application, were an order of magnitude greater than the pyridine concentrations. Detectable

Figure 15. Semilog graphs of 3,5,6-trichloro-2-pyridinyloxyacetic acid (triclopyr) concentrations in vegetation following ground application. Concentrations are expressed as C_t , concentration at time, t , divided by C_i , initial concentration. Graphs are for South (A), Middle (B), and North (C) plots.

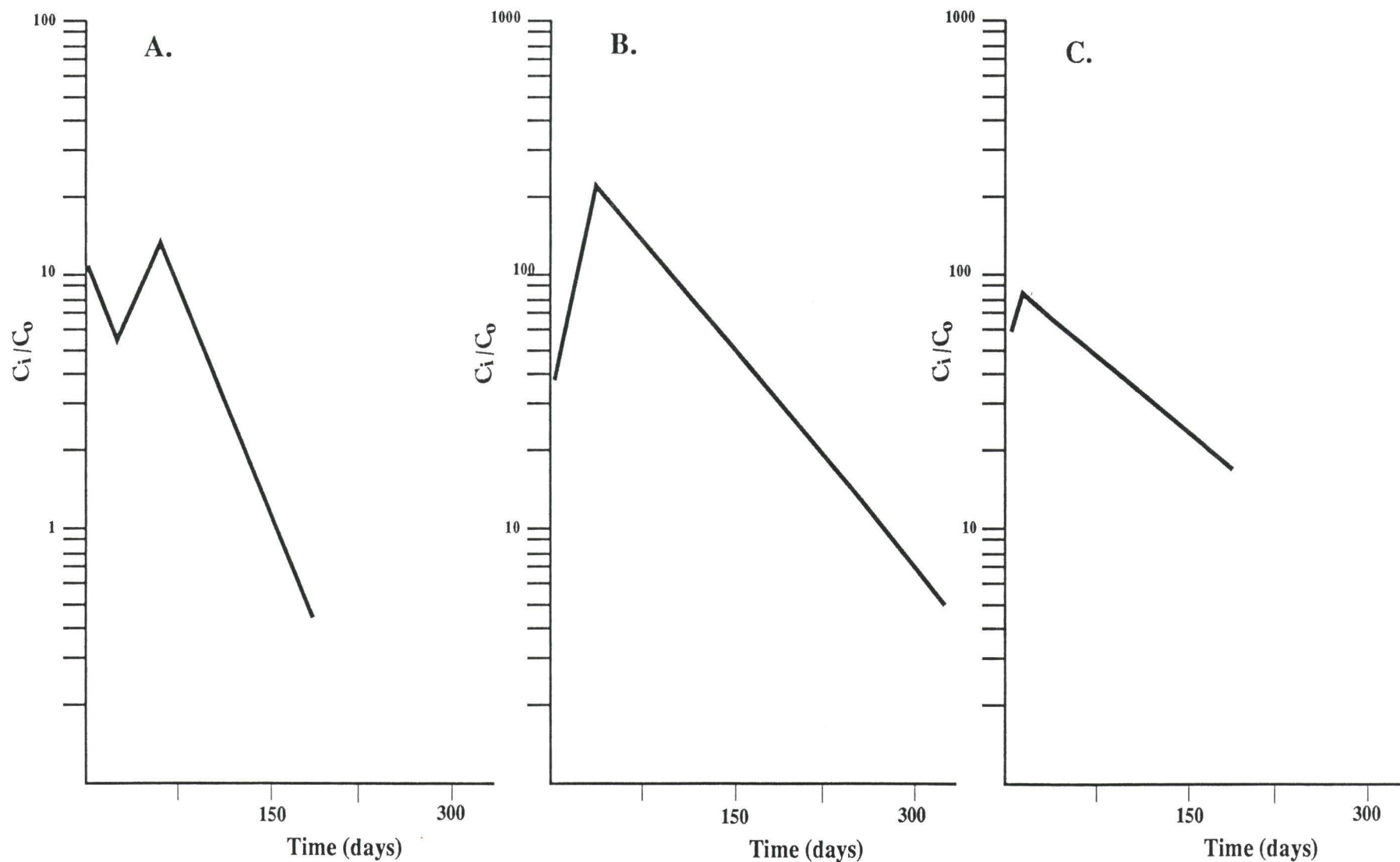


Figure 16. Semilog graphs of 3,5,6-trichloro-2-pyridinol concentrations in vegetation following triclopyr application. Concentrations are expressed as C_t , concentration at time, t , divided by C_i , initial concentration. Graphs are for South (A), Middle (B), and North (C) plots.

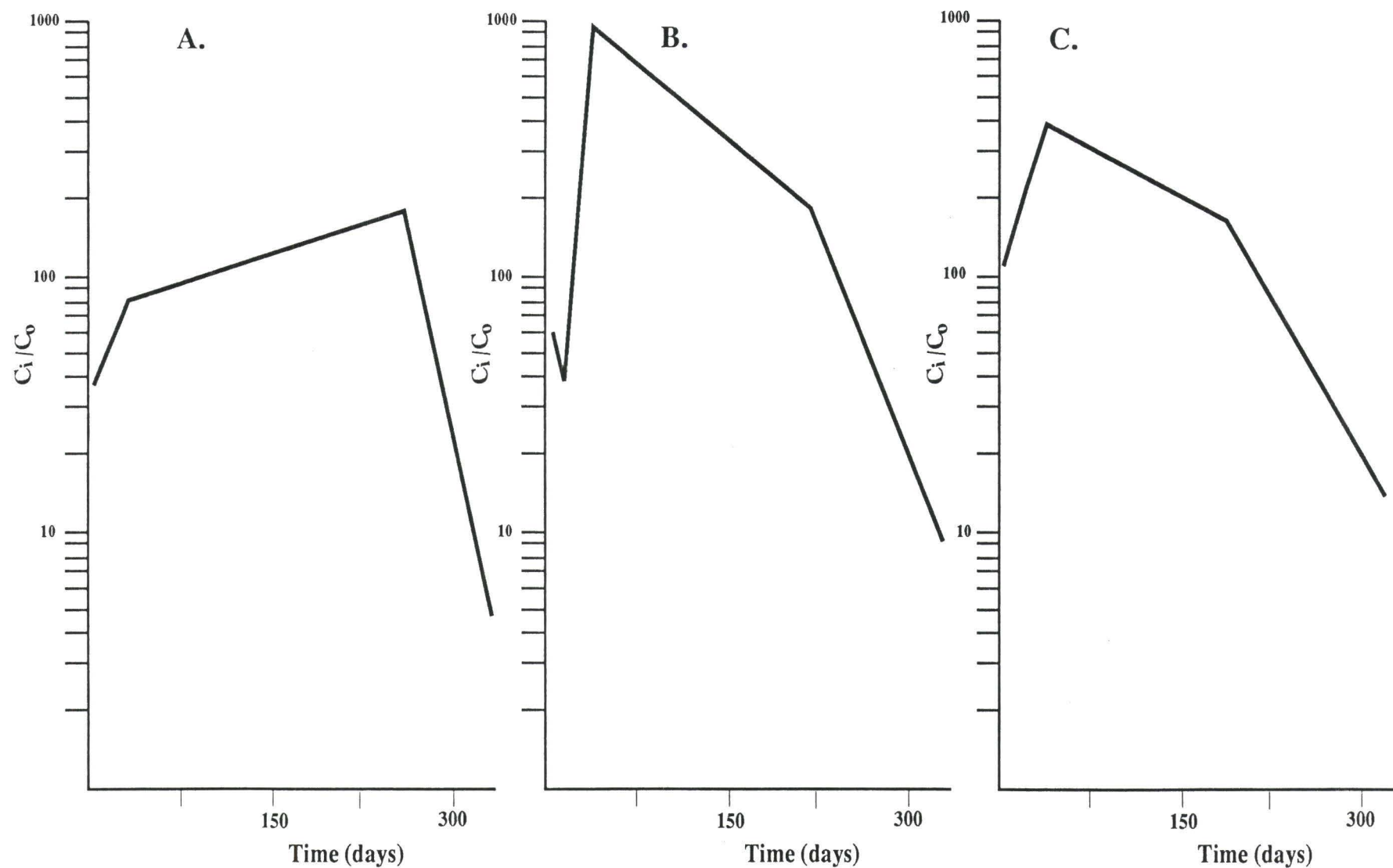
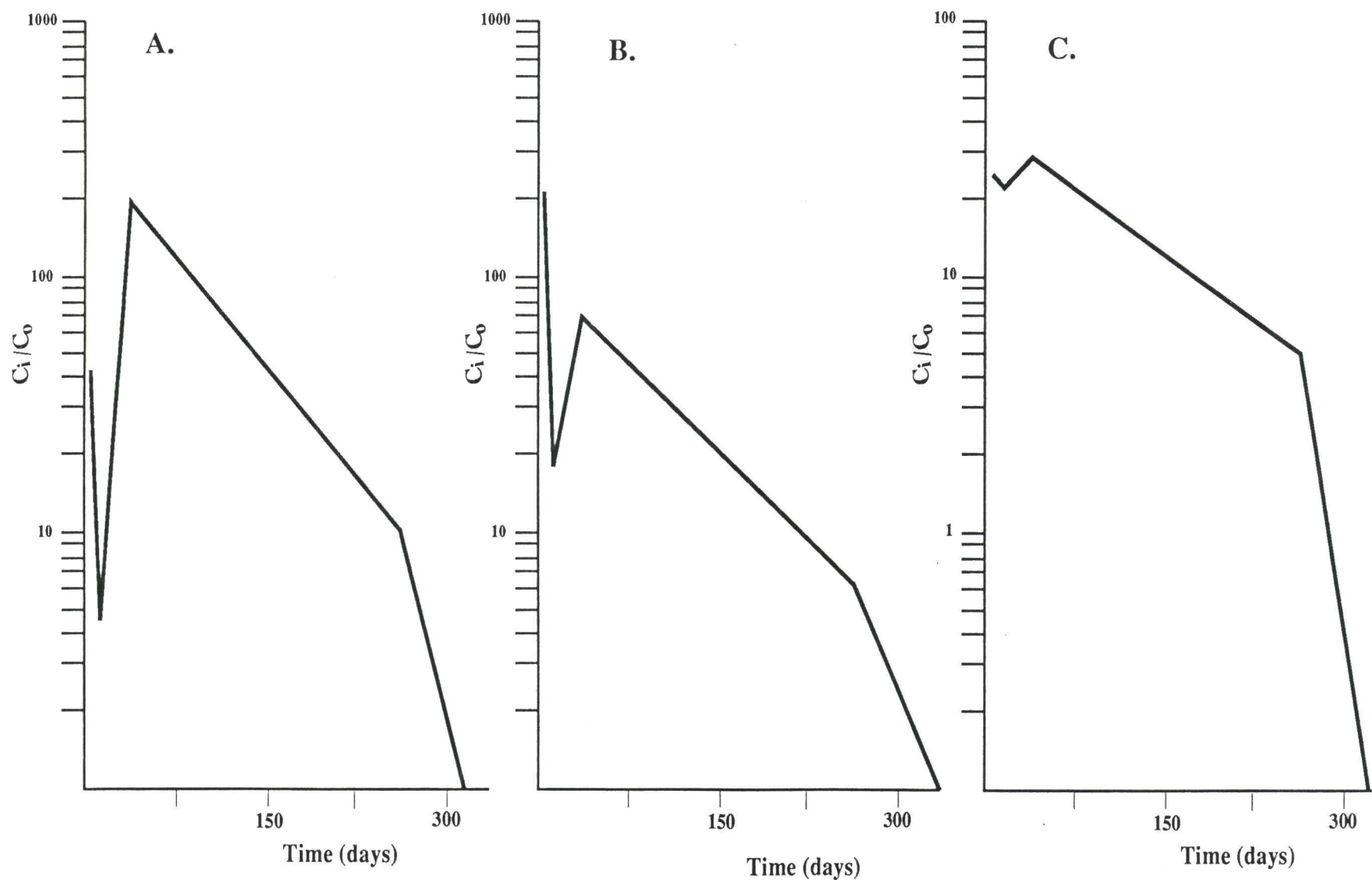


Figure 17. Semilog graphs of 3,5,6-trichloro-2-methoxypyridine concentrations in vegetation following triclopyr application. Concentrations are expressed as C_t , concentration at time, t , divided by C_i , initial concentration. Graphs are for South (A), Middle (B), and North (C) plots.



levels of pyridinol in soils may be reasonably expected for as long as 2 years at sites of triclopyr applications.

Both triclopyr and its pyridine metabolite are environmentally mobile compounds, with relatively high solubilities in water and relatively low soil absorption coefficients. The absence of surface runoff at the study site during the study period precluded monitoring of surface waters for triclopyr and its metabolites. However, because of their mobility, some levels of triclopyr and pyridine may be expected to reach nearby surface waters following normal applications, depending on precipitation, vegetative cover, topography, soil type, and application variables. Pyridinol may be less mobile, which may also contribute to its accumulation in the soil. The application variables affecting the transport to surface waters include herbicide application rate and method, ambient temperature and the use of buffer zones. An ameliorating factor in northern Idaho forest site preparation applications is the fact that the optimum application time for herbicide effectiveness corresponds with a period of low average rainfall. Therefore, herbicide photodecomposition should be maximized and off-site mobility should be minimized. Such operational considerations may be used for other triclopyr applications to maximize herbicide retention on site.

Because the toxicity of triclopyr to fish and some lower aquatic organisms is very low, concentrations resulting in acute or chronic effects on non-target organisms in receiving waters following normal forestry applications are unlikely, even at the higher application rates. This generalization is applied to the triethylamine formulation, Garlon 3A, but must be used for the butoxyethyl ester formulation, Garlon 4, with reservations. The Garlon 3A formulation has apparently an even lower toxicity to fish and some other aquatic test organisms than pure triclopyr. However, the Garlon 4 formulation is very toxic to fish. Although the butoxyethyl ester formulation is much less soluble and is believed to be hydrolyzed rapidly in water, forestry use of Garlon 4 should involve adequate buffer zones and particular care to prevent aquatic contamination. As noted previously timing of applications in dry periods should help prevent off-site movement and impacts.

In addition to the information on triclopyr itself, toxicity data for the metabolites, pyridine and pyridinol, are also needed. Triclopyr has a common breakdown product, trichloropyridinol, with the insecticide, chlorpyrifos, which perhaps should serve to increase the interest and need for data on pyridinol toxicity. The situation where much basic toxicity information has been developed on the parent compound but little information is available on the metabolites is not unusual, espe-

cially for relatively new pesticides. Unfortunately, these data gaps contribute to uncertainties on the environmental consequences of use of what may be environmentally sound materials. Therefore, toxicity data for pyridinol should be developed as soon as possible.

If these compounds do reach surface waters, the lifetimes of both triclopyr and pyridine should be low because of their susceptibility to photodecomposition. However, because hydrolysis is not a major mechanism for decomposition of triclopyr and its metabolites, these compounds may be more persistent in sediments where light penetration and aerobic microbial activity are reduced. Such a phenomenon has been noted for other compounds, such as 2,4-D, which typically hydrolyze rapidly in water, but which may persist for much longer periods of time in sediments. Because triclopyr does not tend to bioaccumulate, persistence in sediments would not be expected to pose a significant environmental problem, although the possible chronic effects of long-term exposures to low concentration levels warrants further attention.

In general, the relative environmental instability of triclopyr reduces the opportunities for off-site exposures to triclopyr during forest site preparation applications. No major deviations from environmental behavior predicted from the chemical and physical characteristics and from previous laboratory and field studies for triclopyr and its breakdown products were noted by this study. The use of triclopyr appears to be environmentally sound if reasonable precautions to minimize off-site impacts are followed during applications.

LITERATURE CITED

- Bovey R. W., H. Hein, Jr., and R. E. Meyer. 1983. Adsorption and translocation of triclopyr in honey mesquite (*Prosopis juliflora* var. *glandulosa*). *Weed Sci.* 29(3):356-361.
- Bovey R. W., H. Hein, Jr., and R. E. Meyer. 1986. Concentration of 2,4,5-T, triclopyr, picloram, and clopyralid in honey mesquite (*Prosopis juliflora*) stem. *Weed Sci.* 34(2):211-217.
- Bovey, R. W., M. L. Ketchersid, and M. G. Merle. 1979. Distribution of triclopyr and picloram in huisache (*Acacia farnesiana*). *Weed Sci.* 27(5):527-531.
- Bovey, R. W. and H. S. Mayeux, Jr. 1980a. Effectiveness and distribution of 2,4,5-T, triclopyr, picloram and 3,6-dichloropicolinic acid in honey mesquite (*Prosopis juliflora* var. *glandulosa*). *Weed Sci.* 28(6):666-670.
- Bovey, R. W. and H. S. Mayeux, Jr. 1980b. Uptake and distribution of 2,4,5-T, triclopyr, picloram and 3,6-dichloropicolinic acid in honey mesquite. *Proc. Ann. Meet. South Weed Sci. Soc.* 33:291. In Weed Abstracts. 1981. 30: Abstract No. 4002.
- Bovey, R. W. and R. E. Meyer. 1981. Effects of 2,4,5-T, triclopyr, and 3,6-dichloropicolinic acid on crop seedlings. *Weed Sci.* 29(3):256-261.
- Bovey, R. W., R. E. Meyer, and J. R. Bauer. 1981. Potential herbicides for brush control. *J. Range Mgt.* 34(2):144-148.
- Boyd, R. J., D. L. Miller, F. A. Kidd, and C. P. Ritter. 1985. Herbicides for forest weed control in the Inland Northwest: A summary of effects on weeds and conifers. General Technical Report INT-195. U.S. Forest Service. U.S. Department of Agriculture. Intermountain Research Station. Ogden, Utah.
- Byrd, B. C., W. G. Wright, and L. E. Warren. 1975. Vegetation control with Dowco 233 herbicide. *Proc. S. Weed Sci. Soc.* 28:251-260.
- Conway, R. A., ed. 1982. *Environmental risk analysis chemistry*. Van Nostrand-Reinhold. New York, NY.
- DOW Chemical Company. 1979. Technical information on triclopyr, The active ingredient of Garlon herbicides. *Technical Data Sheet*. 4pp. The DOW Chemical Company. Midland, Michigan.
- DOW Chemical Company. 1983a. Technical information on triclopyr, The active ingredient of Garlon herbicides. *Technical Data Sheet No. 137-859-483*. The DOW Chemical Company. Midland, Michigan.
- DOW Chemical Company. 1983b. Technical information on triclopyr, The active ingredient of Garlon herbicides. *Technical Data Sheet 137-1639-83*. The DOW Chemical Company. Midland, Michigan.
- Eckerlin, R. H., J. G. Ebel, G. A. Maylin, T. V. Muscato, W. H. Gutenmann, C. A. Bache, and D. J. Lisk. 1987. Excretion of triclopyr in the bovine. *Bull. Environ. Contam. Toxic.* 39:443-447.
- Engle, D. M. and C. D. Bonham. 1980. Nonstructural carbohydrates in roots of Gambel oak sprouts following herbicide treatment. *J. Range Manage.* 33(5):390-394.

- Gersich, F. M., C. G. Mendoza, D. L. Hopkins, and K. M. Bodner. 1984. Acute and chronic toxicity of triclopyr triethylamine salt to *Daphnia magna* Straus. *Bull. Environ. Contam. Toxic.* 32:497-502.
- Getsinger, K. D. and H. E. Westerdahl. 1984. Field evaluation of Garlon 3A (triclopyr) and 14-ACE-B (2,4-D BEE) for control of Eurasian water milfoil. Aquatic plant control research program. Report No. WES/MP/A-84-5. Environmental Laboratories. Army Corps of Engineerings Waterways Experiment Station. Vicksburg, Mississippi.
- Ghassemi, F. M., L. Fargo, P. Painter, S. Quinlivan, R. Scofield, and A. Tanaka. 1981. Environmental fates and impacts of major forest use pesticides. TRW Co., Redondo Beach, CA. pp. A 285-297.
- Goring, C. A. I., D. A. Laskowski, J. W. Hamaker, and R. W. Meikle. 1975. Principles of pesticide degradation in soils. in *Environmental dynamics of pesticides*. Hague and Freed, 1975. pp. 135-172.
- Gorrell, R. M. 1980. Horsenettle root control with selected herbicides: translocation, fate and influence on carbohydrate metabolism. *Dissertation Abstracts International*, B. 40(10):4586-4587.
- Gorrell, R. M., S. W. Bingham, and C. L. Foy. 1979. Movement and fate of dicamba, picloram and triclopyr in horse-nettle (*Solanum carolinense* L.). In: Abstracts of 1979 Meeting of the Weed Science Society of America. pp.56-57.
- Haagsma, T. 1975 Dowco 233 herbicide. Possible new tool in vegetation management. *Down to Earth* 30(4):22-24.
- Hague, R. and V. H. Freed. 1975. *Environmental dynamics of pesticides*. Plenum Press. New York, NY.
- Hamaker, J. W. 1974. Adsorption of 3,5,6- trichloro -2- pyridinol by soils. Report No. GS-1354. cited in Ghassemi et al., 1981.
- Hamaker, J. W. 1975. Adsorption of triclopyr by soils. Report No. GS-1390. cited in Ghassemi et al., 1981.
- Hamaker, J. W. 1976. The hydrolysis of triclopyr in buffered distilled water by soils. Report No. GS-1410. cited in Ghassemi et al., 1981.
- Hamaker, J. W. 1977. Photolysis of triclopyr (3,5,6-trichloro -2- pyridinoxyacetic acid). Report No. GS-1467. cited in Ghassemi et al., 1981.
- Hamaker, J. W. and C. A. I. Goring. 1976. Turnover of pesticide residues in soil. In Kaufman, 1976.
- Hanley, T. R., Jr., D. J. Thompson, A. K. Palmer, R. P. Beliles, and B. A. 1984. Teratology and reproduction studies with triclopyr in rat and rabbit. *Fund. Appl. Toxic.* 4:872-882.
- Holt, J. S. S. R. Radosevich, and W. L. Graves. 1985. Long-term effects of vegetation of herbicide treatments on chapparral. *Weed Sci.* 33(3):353-357.
- Huang, P. M. 1980. Adsorption processes in soil. In: *Reactions and Processes*. O. Huntzinger, ed. 2: Part A.
- Jacoby, P. W. and C. H. Meadows, Jr. 1983. Triclopyr for control of honey mesquite (*Prosopis juliflora*). *Weed Sci.* 31:681-685.

- Jacoby, P. W. and C. H. Meadows, Jr. 1984. Grazon ET herbicide for control of honey mesquite. *Down to Earth* 40(1):7-11.
- Johnson, W. W. and M. T. Finley. 1980. *Handbook of acute toxicity of chemicals to fish and aquatic invertebrates*. Fish and Wildlife Service Resource Publication 137. U. S. Department of Interior. Washington, D. C.
- Kaufman, D. D., G.G. Still, G. D. Paulson, and S. K. Bandal. 1976. *Bound and conjugated pesticide residues*. ACS Symposium Series. American Chemical Society. Washington, D. C.
- Kenaga, E. E. 1980. Correlation of bioconcentration factors of chemicals in aquatic and terrestrial organisms with their physical properties. *Env. Sci. Tech.* 14(5):553-556.
- King, E. J. and S. R. Radsosovich. 1979. Tanoak (*Lithocarpus densiflorus*) leaf surface characteristics and absorption of triclopyr. *Weed Sci.* 27(8):509-604.
- King, E. J., R. D. Fears, and L. E. Warren. 1983. Invert emulsions of Garlon herbicides. *Down to Earth* 39(1):22-26.
- Knisel, W. C. ed. 1980. CREAMS: A field scale model for chemicals, runoff, and erosion in agricultural management systems. USDA Cons. Res. Rep. No. 26.
- Laskowski, D. A., C. A. I. Goring, P. J. McCall, and R. L. Swann. 1982. Terrestrial environment. in Conway, 1982. pp. 198-240.
- Leonard, R. A. and J. D. Nowlin. 1980. The pesticide submodel. in Knisel, 1980.
- McCall et al. 1976. Degredation of ¹⁴C-triclopyr in sterile and non-sterile soil. cited in Ghessemi et al., 1986.
- McCall, P. J. and P. D. Gavit. 1986. Aqueous photolysis of triclopyr and its butoxy ethyl ester and calculated environmental photodecomposition rates. *Environ. Toxicol. Chem.* 5:879-885.
- McCall, P. J. and R. L. Swann. 1978. Nitrapyrin volatility in soil. *Down to Earth* 34:21-27.
- McCormack, M. L. 1979. General summary of forest uses of herbicides in northern New England. *Proc. Ann. Meet. NE. Weed Sci. Soc.* 33(suppl.):45-46.
- McKellar, R. L. 1977a. Determination of triclopyr ([3,5,6-trichloro-2-pyridinyl]oxy]acetic acid); 3,5,6-trichloro-2-pyridinol and 2-methoxy-3,5,6-trichloropyridine in grass by gas chromatography. Dow Method ACR 77.4. Dow Chemical Company. Midland, MI.
- McKellar, R. L. 1977b. Determination of triclopyr ([3,5,6-trichloro-2-pyridinyl]oxy]acetic acid); 3,5,6-trichloro-2-pyridinol and 2-methoxy-3,5,6-trichloropyridine in soil by gas chromatography. Dow Method ACR 77.5. Dow Chemical Company. Midland, MI.
- McKellar, R. L. 1977c. Residues of triclopyr, 3,5,6-trichloro-2-pyridinol, and 3,5,6-trichloro-2-methoxypyridine. Report No. GH-C-983. cited in Ghassemi et al., 1981.
- McKellar, R. L. and W. C. Brown. 1984. Determination of triclopyr and 3,5,6-trichloro-2-pyridinol in soil by gas chromatography. Dow Method ACR 84.2. Dow Chemical Company. Midland, MI.
- McKellar, R. L., O. Schubert, B. C. Boyd, L. P. Stevens, and E. J. Norton. 1982. Aerial application of Garlon 3A herbicide to a West Virginia watershed. *Down to Earth* 38(2):15-19.

- Marshall, W. K. and J. R. Roberts. 1978. *Ecotoxicity of chloropyrifos*. National Research Council of Canada. NRC Associate Committee on Scientific Criteria for Environmental Quality. Subcommittee on Pesticides and Related Compounds. Ministry of the Environment. Ontario, Canada.
- Mayes, M. A., D. C. Dill, K. M. Bodner, and C. G. Mendoza. 1984. Triclopyr triethylamine salt toxicity to life stages of the fathead minnow (*Pimephales promelas rafinesque*). *Bull. Environ. Contam. Toxicol.* 33:339-347.
- Meyer, R. E. and R. W. Bovey. 1985. Response of honey mesquite and understory vegetation to herbicides. *Weed Sci.* 33(4):537-543.
- Miller, D. L. and W. W. Pope. 1981. Preliminary evaluation of Garlon 4 herbicide. Forestry Research Note RN-81-1. Potlatch Corporation. Lewiston, Idaho.
- Miller, D. L. and W. W. Pope. 1982a. Effects of Garlon 4, 2,4-D and Velpar herbicides on north Idaho shrubs. Forestry Research Note RN-82-2. Potlatch Corporation. Lewiston, Idaho.
- Miller, D. L. and W. W. Pope. 1982b. The effects of Garlon 3A and Garlon 4 on north Idaho conifers and shrubs. Forestry Research Note RN-82-3. Potlatch Corporation. Lewiston, Idaho.
- Miller, D. L. and W. W. Pope. 1983. Effects of Garlon 4, 2,4-D, and Velpar herbicides on north Idaho shrubs. Forestry Research Note RN-83-7. Potlatch Corporation. Lewiston, Idaho.
- Molnar, J. S. Daru, A. Fulop, and S. Gedeon. 1983. Study of the percolation of triclopyr into the soil by bioassay and analytical methods. In *Weed Abstracts*. 34(1): Abs. No. 116.
- National Oceanic and Atmospheric Administration. 1986. Climatological data annual summary: Idaho: 1986. 89(13). National Satellite, Data, and Information Service. Asheville, North Carolina.
- National Oceanic and Atmospheric Administration. 1987. Climatological data monthly summary: Idaho: 1987. 90(1 to 4). National Satellite, Data, and Information Service. Asheville, North Carolina.
- Nilsson, H. 1983. Persistence and mobility of herbicides in arable soil. Investigations in 1980-1981. *Proc. 24th Swedish Conf. Weeds and Weed Cont.* 2:393-399.
- Norris, L. A., M. L. Montgomery, and L. E. Warren. 1981. Efficacy and environmental behavior of triclopyr in western Oregon. Oregon Forest Research Laboratory Technical Paper No. 1939.
- Norris, L. A., M. L. Montgomery, and L. E. Warren. 1987. Triclopyr persistence in western Oregon hill pastures. *Bull. Environ. Contam. Toxic.* 39:134-141.
- Nutter, W. L., T. Tkacs, P. B. Bush, and D. G. Neary. 1984. Simulation of herbicide concentrations in stormflow from forested watersheds. *Water Res. Bull.* 20(6):851-857.
- Radosevich, S. R. and D. E. Bayer. 1979. Effect of temperature and photoperiod on triclopyr, picloram, and 2,4,5-T translocation. *Weed Sci.* 27(1):22-27.
- Regoli, A. J. and D. A. Laskowski. 1974. Aerobic decomposition rates of ring labeled 14C-3,5,6-trichloro -2- pyridyl oxyacetic acid in soil. Report GS-1364. cited in Ghassemi et al., 1981.
- Sassman, J., R. Pietra, M. Jacobs, and J. Cioffi. 1984. Pesticide background statements. Vol. I. Herbicides. Agriculture Handbook No. 633. U.S. Forest Service. U.S. Department of Agriculture. Washington, D. C.
- Servizi, J. A., R. W. Gordon, and D. W. Martens. 1987. Acute toxicity fo Garlon 4 and Roundup herbicides to salmon, *Daphnia*, and trout. *Bull. Environ. Contam. Toxicol.* 39:15-22.

- Siltanen, H., C. Rosenberg, M. Raatikainen, and T. Raatikainen. 1981. Triclopyr, glyphosate, and phenoxyherbicide residues in cowberries. *Bull. Environ. Contam. Toxicol.* 27:731-737.
- Swann, R. L., P. J. McCall, and S. M. Unger. 1979. Volatility of pesticides from soil surfaces. Proc. 177th Nat. Meet. Amer. Chem. Soc., cited in Laskowski et al., 1982.
- Torstensson, L. and J. Stark. 1982. Persistence of triclopyr in forest soils. *Proc. 23rd Swedish Conf. Weeds and Weed Cont.* . 1:302-310.
- Tsukoika, T., R. Takeshita, and T. Murakami. 1984. Gas chromatographic determination of triclopyr in environmental waters. *Analyst.* 111(2):145-149.
- Wan, M. T., D. J. Maul, R. G. Watts. 1987. Acute toxicity to juvenile Pacific salmonides of Garlon 3A, Garlon 4, triclopyr, triclopyr ester, and their transformation products: 3,5,6-trichloro-2-pyridinol and 2-methoxy-3,5,6-trichloropyridine. *Bull. Environ. Contam. Toxicol.* 39:721-728.
- Weed Science Society of America. 1983. *Herbicide handbook*. 5th edition. Champaign, Illinois.
- Worthing, C. R., ed. 1983. *Pesticide manual*. 7th ed. Lavenham Press. Suffolk, Great Britian.

Appendix: Tables

Table A-1. Measured concentrations of triclopyr and metabolites in soil samples from the South plot. (All concentrations are in mg/kg-soil, dry weight.)

Date	Triclopyr	Pyridine	Pyridinol
10-7-86	2.8589	0.0876	0.1232
10-9-86	0.5230	0.1447	0.2117
10-15-86	0.4344	0.351	0.2975
10-21-86	0.0037		0.2335
4-4-87	0.0174	0.0023	0.1627

Table A-2. Measured concentrations of triclopyr and metabolites in soil samples from the Middle plot. (All concentrations are in mg/kg-soil, dry weight.)

Date	Triclopyr	Pyridine	Pyridinol
10-7-86	4.6360	0.2201	0.0785
10-9-86	3.2063	0.0595	0.2111
10-15-86	0.6118	0.0597	0.2117
10-21-86	0.1380	0.0093	0.2073
4-4-87	0.0857	0.0049	0.2380

Table A-3. Measured concentrations of triclopyr and metabolites in soil samples from the North plot. (All concentrations are in mg/kg-soil, dry weight.)

Date	Triclopyr	Pyridine	Pyridinol
10-7-86	0.2208	0.0179	0.3492
10-9-86	0.2559	0.0122	0.0978
10-15-86	0.1117	0.0229	0.1808
10-21-86	0.4037	0.0263	0.4956
4-4-87	0.009	0.0017	0.1912

Table A-4. Concentrations of triclopyr in soil profile samples collected on May 25, 1987. (All values are in mg/g-soil. nd = not detected, D₀ = top 2 cm, 1 = 2 to 10 cm horizon, 2 = 10 to 20 cm horizon, 3 = 20 to 30 cm horizon, and 4 = 30 to 40 cm horizon.)

<i>Plot</i>	<i>Depth</i>			<i>^{av}X</i>
North	D ₀	1.790	0.620	0.401
	1	0.438	0.280	0.359
	2	0.349	nd	0.175
	3	0.386	nd	0.193
	4	0.479	nd	0.240
Middle	D ₀	2.822	—	2.822
	1	0.470	0.078	0.274
	2	0.191	0.172	0.182
	3	0.117	0.595	0.356
	4	0.112	0.168	0.140
South	D ₀	0.994	—	0.994
	1	0.302	2.071	1.187
	2	0.239	7.419	3.829
	3	0.257	2.893	1.575
	4	0.344	0.344	0.344

Table A-5. Concentrations of pyridinol in soil profile samples collected on May 25, 1987. (All values are in mg/g-soil. nd = not detected, D₀ = top 2 cm, 1 = 2 to 10 cm horizon, 2 = 10 to 20 cm horizon, 3 = 20 to 30 cm horizon, and 4 = 30 to 40 cm horizon.)

<i>Plot</i>	<i>Depth</i>			<i>X</i> _{av}
North	D ₀	0.105	0.058	0.082
	1	0.031	0.020	0.026
	2	nd	0.015	0.008
	3	0.061	0.016	0.039
	4	0.029	0.006	0.018
Middle	D ₀	1.293	—	1.293
	1	0.149	0.032	0.091
	2	0.020	0.143	0.082
	3	0.091	0.149	0.120
	4	nd	0.056	0.028
South	D ₀	0.222	4.635	2.429
	1	0.034	1.628	0.831
	2	0.069	1.840	0.955
	3	0.026	0.988	0.507
	4	0.009	0.172	0.091

Table A-6. Concentrations of pyridine in soil profile samples collected on May 25, 1987. (All values are in mg/g-soil. nd = not detected, D₀ = top 2 cm, 1 = 2 to 10 cm horizon, 2 = 10 to 20 cm horizon, 3 = 20 to 30 cm horizon, and 4 = 30 to 40 cm horizon.)

<i>Plot</i>	<i>Depth</i>			$\bar{X}$
North	D ₀	0.027	0.021	0.024
	1	0.029	0.004	0.017
	2	0.025	0.006	0.016
	3	0.032	0.008	0.020
	4	0.034	nd	0.017
Middle	D ₀	0.144	0.063	0.104
	1	0.039	0.027	0.033
	2	0.031	0.017	0.024
	3	0.047	0.026	0.037
	4	0.006	0.004	0.005
South	D ₀	0.048	0.193	0.121
	1	0.010	0.140	0.075
	2	0.030	0.101	0.066
	3	0.022	0.048	0.035
	4	0.017	0.008	0.013

Table A-7. Measured concentrations of triclopyr and metabolites in soil samples from the South plot. (All concentrations are in mg/kg-soil, dry weight.)

Date	Triclopyr	Pyridine	Pyridinol
10-7-86	4653.2	2.1815	0.4247
10-9-86	983.2	1.2465	0.2419
10-15-86	59.7	0.0530	0.3457
10-21-86	386.7	6.0255	
4-4-87	28.1	0.4375	1.2346
5-25-87	nd	0.0005	nd
8-16-87	nd	nd	0.0074

Table A-8. Measured concentrations of triclopyr and metabolites in soil samples from the Middle plot. (All concentrations are in mg/kg-soil, dry weight.)

Date	Triclopyr	Pyridine	Pyridinol
10-7-86	1298.8	4.827	4.1975
10-9-86	106.3	0.336	0.0740
10-15-86	1815.3	1.525	0.6543
10-21-86	3791.0	4.153	11.1111
4-4-87	35.5	0.150	1.8518
5-25-87	129.3	0.030	0.6170
8-16-87		nd	0.001 nd

Table A-9. Measured concentrations of triclopyr and metabolites in soil samples from the North plot. (All concentrations are in mg/kg-soil, dry weight.)

Date	Triclopyr	Pyridine	Pyridinol
10-7-86	223.3	0.947	0.1560
10-9-86	158.4	0.410	0.1850
10-15-86	300.4	0.427	0.1970
10-21-86	194.0	0.309	0.6790
4-4-87	49.4	0.056	0.0864
5-25-87	nd	nd	0.0222
8-16-87		nd	0.001 0.0444